Electronic Supplementary Information

DDQ-promoted Dehydrogenation from Natural Rigid Polycyclic Acids or Flexible Alkyl Acids to Generate Lactones by a Radical Ion Mechanism

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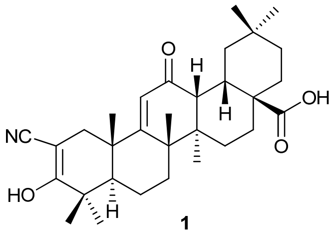
1. General information

Melting points were determined via a capillary apparatus (RDCSY-I) and are reported directly. All the synthesized compounds were purified by column chromatography (CC) on silica gel by Isolera-One flash purification system from Biotage. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 plates (250μm; Qingdao Ocean Chemical Company, China). The products were analyzed by ^{1}H NMR and ^{13}C NMR (Bruker ACF-300Q, 300 M Hz), MS (Hewlett-Packard 1100 LC/MSD spectrometer), IR (Nicolet iS10 FT-IR), HRMS (Waters Q-TOF Micro^{TM}). The X-ray diffraction analyses were performed on a Nonius CAD4 diffractometer and incident beam graphite monochromator using a Mo sealed tube source (λ) 0.71073 Å). ESR spectra were recorded on Bruker EMX 10/12 ESR SPECTROMETER. Compounds **18**, **26** and DPPH (98%) were purchased from Tokyo Chemical Industry Co. Ltd; compounds **20**, **22** and **24** (98%) were purchased from Wuxi Pharmaxyn Laboratories Ltd; compound **1**, **6**, **28**, **29** and **30** were synthesized according to literature[1]. Oleanolic acid, ursolic acid and other reagents were purchased from Shanghai Chemical Reagent Company. The purchased compounds were used without further purification.

2. Preparation and characterization of compounds



1

2-Cyano-3-hydroxy-12-oxoolean-2(3),9(11)-dien-28-oate (1)

The title compound **1** was synthesized according to literature[1].

m.p. 198-200 °C;

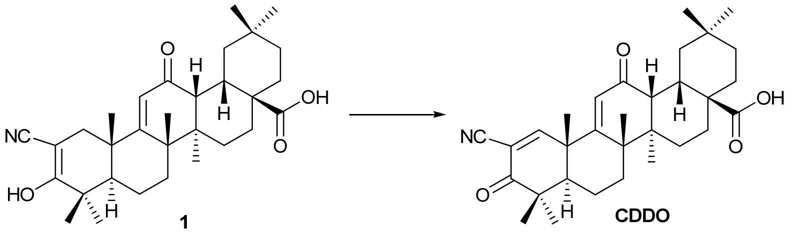
IR (KBr, cm^{-1}): 3468, 3186, 2949, 2868, 2208, 1709, 1636, 1467, 1385, 1366;

ESI-MS: 492 [M-H]$^-$;

^{1}H NMR (300M Hz, CDCl$_3$, 25 °C, TMS): δ 5.7 (s, 1H), 3.04 (m, 1H), 2.96 (d, J = 4.5 Hz, 1H), 2.41 (d, J = 9.0 Hz, 1H), 2.26 (d, J = 9.0 Hz, 1H), 1.26, 1.21, 1.24, 1.20, 1.16, 1.00, 0.91 (s, each 3H) ppm;

^{13}C NMR (75M Hz, CDCl$_3$, 25 °C, TMS): δ 199.8, 183.6, 175.4, 171.8, 124.3, 118.9, 78.5, 49.7, 48.4, 47.1, 45.3, 42.1, 41.8, 38.7, 38.6, 38.3, 35.7, 34.4, 33.2, 32.9, 31.4, 31.2, 30.7, 28.3, 28.0, 23.9, 23.0, 22.5, 21.9, 19.8, 14.1 ppm;

HRMS (EI$^+$) calc. for $[C_{31}H_{44}NO_4]^+$ 494.3270, found 494.3288.



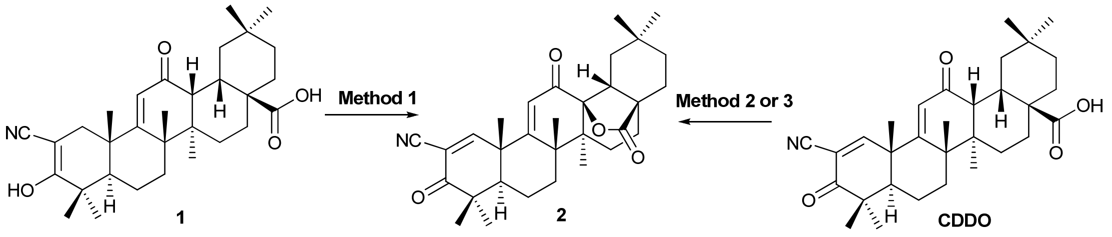
2-Cyano-3,12-dioxooleana-1,9(11)-dien-28-oate (CDDO)

A mixture of **1** (0.25 g, 0.51 mmol) and DDQ (0.12 g, 0.51 mmol) in anhydrous benzene (20 mL) was refluxed for 15 min. After filtration, the filtrate was evaporated in vacuo to give a residue, which was subjected to flash column chromatography (petroleum ether/EtOAc) to give CDDO as an amorphous solid (0.23 g, 91%). The title compound was known as CAS 218600-44-3.[2]

m.p. 180-182 °C;

ESI-MS: 490 $[M-H]^-$, 492 $[M+H]^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 8.05 (1H, s), 5.99 (1H, s), 3.03-2.98 (2H, m), 1.55,1.38, 1.34, 1.22, 1.00, 0.91, 0.85 (each 3H,s ,CH_3) ppm.



2-Cyano-3,12-dioxoolean-1,9(11)-dien-28,13*β*-olide (2)

Method 1: A mixture of **1** (0.3 g, 0.61 mmol) and DDQ (0.28 g, 1.22 mmol) in anhydrous benzene (30 mL) was refluxed for 48 h. After filtration, the filtrate was evaporated in vacuo to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc) to give **2** as an amorphous solid (0.17 g, 58%).

Method 2: A mixture of CDDO (0.22 g, 0.45 mmol) and DDQ (0.10 g, 0.45 mmol) in anhydrous benzene (30 mL) was refluxed for 48 h. After filtration, the filtrate was evaporated in vacuo to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc) to give **2** as an amorphous solid (0.12 g, 82%), and 0.07 g of CDDO was recovered.

Method 3: A mixture of CDDO (0.25 g, 0.51 mmol) and DPPH• (0.40 g, 1.02 mmol) in anhydrous benzene (30 mL) was refluxed for 48 h. After filtration, the filtrate was evaporated in vacuo to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc) to give **2** as an amorphous solid (0.20 g, 81%).

m.p. 260-262 °C;

$[\alpha]_D^{25}$ 63.1 (*c* 1.0, in CH_2Cl_2);

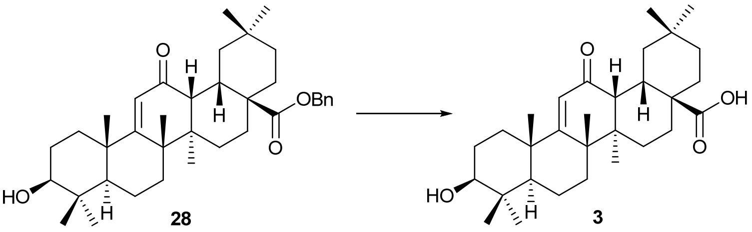
IR (KBr, cm^{-1}): 3434, 2955, 2926, 2855, 2230, 1776, 1735, 1693, 1675, 1617;

ESI-MS: 490 $[M+H]^+$;

^1H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 8.02 (s, 1H), 6.22 (s, 1H), 3.00 (m, 1H), 1.93,1.56, 1.54, 1.46, 1.44, 1.14, 0.98 (s, each 3H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 196.3, 191.2, 178.2, 173.6, 165.4, 123.1, 115.0, 114.3, 87.5, 47.9, 46.4, 45.1, 44.1, 43.5, 42.9, 42.0, 36.6, 34.0, 33.1, 32.7, 31.6, 30.7, 27.6, 27.3, 27.1, 25.8, 23.8, 22.8, 21.5, 20.1, 17.5 ppm;

HRMS (EI^+) calc. for $[C_{31}H_{40}NO_4]^+$ 490.2957, found 490.2961.



3β-Hydroxy-12-oxoolean-9(11)-en-28-oate (3)

A solution of **28** (2.0 g, 3.57 mmol) in THF (30 mL) was treated with 10% Pd/C (0.2 g). The mixture was stirred at RT with H_2 at atmospheric pressure for 1-2 h. The mixture was filtered through celite, and a filter cake was washed with THF. The filtrate was concentrated in vacuo to give a solid, which was subjected to flash column chromatography (petroleum ether/EtOAc) to give **3** as an amorphous solid (1.63 g, 97%).

m.p. 294-296 °C;

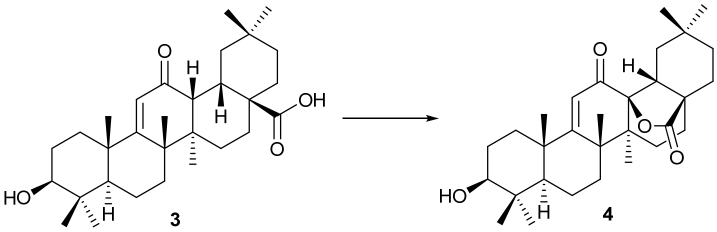
IR (KBr, cm^{-1}): 3443, 2927, 2869, 1710, 1687, 1661, 1593, 1466, 1384, 1363;

ESI-MS: 469 $[M-H]^-$;

^1H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 5.76 (s, 1H), 3.25 (m, 1H), 3.02 (m, 1H), 2.90 (d, *J* = 4.5 Hz, 1H), 1.25, 1.17, 1.03, 1.00, 1.00, 0.89, 0.83 (s, each 3H) ppm;

^{13}C NMR (75M Hz, CDCl$_3$, 25 °C, TMS): δ 200.4, 183.5, 178.4, 122.7, 78.1, 50.2, 49.5, 47.1, 45.3, 41.7, 40.0, 39.2, 36.4, 35.8, 34.5, 33.2, 33.0, 32.9, 31.5, 30.7, 29.7 , 28.1, 27.4, 23.8, 23.7, 23.1, 22.6, 21.7, 18.0, 15.5 ppm;

HRMS (EI$^+$) calc. for [$C_{30}H_{47}NO_4$]$^+$ 471.3474, found 471.3482.



3β-Hydroxy-12-oxoolean-9(11)-en-28,13*β*-olide (4)

Compound **4** was synthesized from **3** (0.5 g, 1.06 mmol) according to the synthetic procedure of **2** (method 2), giving an amorphous solid (0.30 g, 82%), and 0.13 g of **3** was recovered.

m.p.230-232 °C;

$[\alpha]_D^{25}$ 54.9 (*c* 1.0, in CH$_2$Cl$_2$);

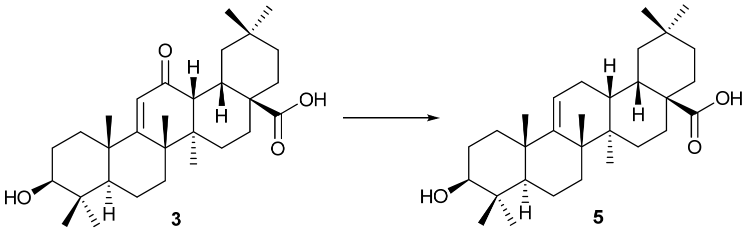
IR (KBr, cm^{-1}): 3324, 2953, 2867, 1777, 1671, 1588, 1467, 1387, 1366, 1292;

ESI-MS: 469 [M+H]$^+$;

^{1}H NMR (300M Hz, CDCl$_3$, 25 °C, TMS): δ 6.0 (s, 1H), 3.24 (m, 1H), 2.98 (m, 1H), 1.52, 1.26, 1.12, 1.00, 0.96, 0.96, 0.85 (s, each 3H) ppm;

^{13}C NMR (75M Hz, CDCl$_3$, 25 °C, TMS): δ 192.3, 184.0, 178.7, 121.6, 87.9. 77.8, 50.2, 46.0, 43.9, 43.5, 41.7, 40.4, 39.3, 36.7, 36.4, 34.1, 34.0, 33.1, 31.6, 30.0, 28.1, 27.4, 27.2, 25.8, 24.4, 23.8, 23.1, 20.2, 17.3, 15.6 ppm;

HRMS (EI$^+$) calc. for [$C_{30}H_{45}O_4$]$^+$ 469.3318, found 469.3342.



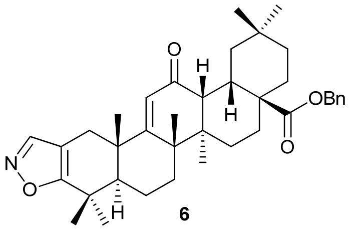
3β-Hydroxyolean-9(11)-en-28-oate (5)

A mixture of **3** (0.5 g, 1.06 mmol), KOH (5.36 g, 95.7 mmol) and hydrazine hydrate (98%) (6.2 mL, 191.4 mmol) in diethylene glycol (50 mL) was refluxed for 1.5 h. After removal of water and hydrazine hydrate, the mixture was then refluxed for additional 6 h. After cooling to the RT, the mixture was neutralized with dilute aqueous HCl and poured into water. A precipitate was obtained by filtration and purified by silica gel column chromatography (petroleum ether/EtOAc) to give **5** (CAS 112899-58-8) as an amorphous solid (0.30 g, 62.1%).

m.p. >275 °C (Lit[2]. >275 °C);

ESI-MS: 455 $[M-H]^-$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 5.57 (m, 1H), 3.22 (m, 1H), 1.14, 1.11, 0.98, 0.94, 0.93, 0.89, 0.78 (each 3H, s).



6

Benzyl 12-oxoisoxazolo[4,5-b]olean-9(11)-en-28-oate (6)

Compound **6** was synthesized according to literature[1].

m.p. 74-76 °C;

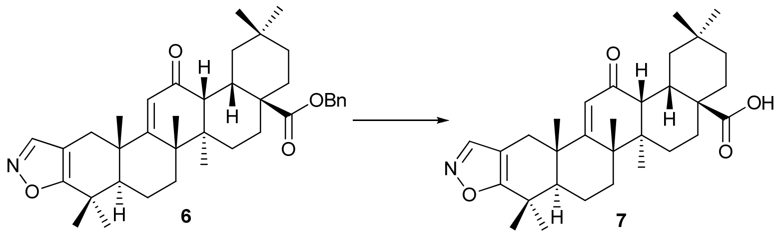
IR (KBr, cm^{-1}): 3434, 2947, 2861, 2353, 2312, 1722, 1660, 1581, 1456, 1384;

ESI-MS: 584 $[M+H]^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 8.06 (s, 1H), 7.38-7.28 (m, 5H), 5.8 (s, 1H), 5.20 (d, *J* = 12.6 Hz, 1H), 5.15 (d, *J* = 12.6 Hz, 1H), 3.10 (m, 1H), 2.80 (d, *J* = 4.5 Hz, 1H), 2.75 (d, *J* = 15 Hz, 1H), 3.38 (d, *J* = 15 Hz, 1H), 1.37, 1.26, 1.12, 1.01, 0.99, 0.95, 0.90 (s, each 3H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 199.8, 177.4, 176.0, 172.1, 150.2, 136.3, 128.6, 128.6, 128.5,128.5, 128.1, 124.5, 108.6, 66.2, 49.8, 49.5, 47.2, 45.6, 41.8, 41.3, 36.0, 35.2, 34.6, 33.7, 33.3, 32.9, 31.6, 31.3, 30.7, 28.8, 28.2, 24.6, 23.2, 22.8, 22.8, 21.6, 21.4, 18.3 ppm;

HRMS (EI^+) calc. for $[C_{38}H_{50}NO_4]^+$ 584.3740, found 584.3763.



12-Oxoisoxazolo[4,5-b]olean-9(11)-en-28-oate (7)

Compound **7** was synthesized from **6** (1.0 g, 1.72 mmol) according to the synthetic procedure of **3**, giving an amorphous solid (0.74 g, 87%).

m.p. 224-226 °C;

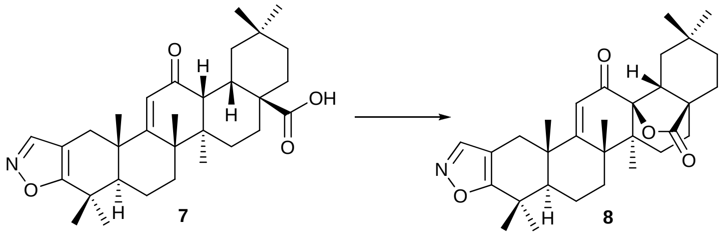
IR (KBr, cm^{-1}): 3455, 2939, 2867, 1706, 1659, 1632, 1478, 1454, 1384,1342;

ESI-MS: 492[M-H]$^{-}$;

^{1}H NMR (300M Hz, CDCl$_3$, 25 °C, TMS): δ 8.06 (s, 1H), 5.9 (s, 1H), 3.06 (m, 1H), 2.93 (d, *J* = 4.5 Hz, 1H), 2.78 (d, *J* = 15.3 Hz, 1H), 2.40 (d, *J* = 15.3 Hz, 1H), 1.35, 1.31, 1.26, 1.16, 1.01, 0.97, 0.85 (s, each 3H) ppm;

^{13}C NMR (75M Hz, CDCl$_3$, 25 °C, TMS): δ 199.8, 183.8, 176.1, 172.1, 150.1, 124.5, 108.5, 49.7, 49.6, 47.1, 45.7, 41.8, 41.3, 35.8, 35.1, 34.5, 33.6, 33.2, 33.0, 31.4, 31.3, 30.6, 28.8, 28.2, 24.5, 23.1, 23.0, 22.6, 21.5, 21.4, 18.2 ppm;

HRMS (EI^{+}) calc. for $[C_{31}H_{44}NO_4]^+$ 494.3270, found 494.3290.



12-Oxoisoxazolo[4,5-b]olean-9(11)-en-28,13*β*-olide (8)

Compound **8** was synthesized from **7** (0.5 g, 1.01 mmol) according to the synthetic procedure of **2** (method 2), giving an amorphous solid (0.36 g, 89%), and 0.09 g of **7** was recovered.

m.p. 278-280 °C;

$[\alpha]_D^{25}$ 64.3 (*c* 1.0, in CH$_2$Cl$_2$);

IR (KBr, cm^{-1}): 3539, 3493, 2945, 2860, 1777, 1669, 1596, 1482, 1467, 1456;

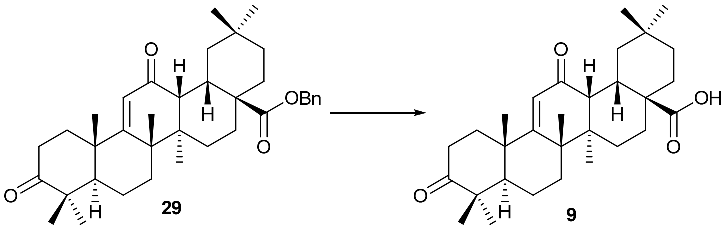
ESI-MS: 492 [M+H]$^{+}$;

^{1}H NMR (300M Hz, CDCl$_3$, 25 °C, TMS): δ 8.08 (s, 1H), 6.13 (s, 1H), 3.01 (m, 1H), 2.85 (d, *J* = 15.0

Hz, 1H), 2.43 (d, *J* = 15.0 Hz, 1H), 1.57, 1.26, 1.61, 1.09, 1.06, 1.00, 0.94 (s, each 3H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 191.9, 181.6, 178.3, 171.9, 150.0, 123.2, 108.2, 87.7, 49.6, 46.3, 44.0, 43.5, 41.8, 41.6, 36.6, 35.2, 34.0, 33.6, 33.1, 32.4, 31.6, 29.5, 28.8, 27.2, 25.9, 25.0, 23.8, 23.1, 21.3, 20.2, 17.4 ppm;

HRMS (EI$^+$) calc. for $[C_{31}H_{42}NO_4]^+$ 492.3114, found 490.3108.



3,12-Dioxoolean-9(11)-en-28-oate (9)

Compound **9** was synthesized from **29** (2.0 g, 3.58 mmol) according to the synthetic procedure of **3**, giving an amorphous solid (1.63 g, 97%).

m.p. 264-268 °C;

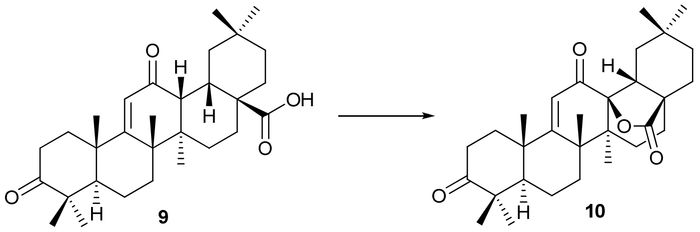
IR (KBr, cm^{-1}): 3462, 2951, 2869, 1726, 1707, 1661, 1593, 1465, 1384, 1366;

ESI-MS: 469 $[M+H]^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 5.8 (s, 1H), 3.04 (m, 1H), 2.94 (d, *J* = 4.5 Hz, 1H), 2.66, 2.49, 2.22 (m, each 1H), 1.30, 1.29, 1.25,1.23, 1.19, 1.13, 1.09 (s, each 3H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 215.8, 199.8, 183.4, 176.6, 124.1, 50.9, 49.6, 47.5, 47.1, 45.4, 41.8, 39.4, 37.0, 35.8, 34.5, 34.1, 33.2, 32.9, 32.0, 31.5, 30.6, 28.1, 26.3, 23.8, 23.7, 23.1, 22.6, 21.6, 21.4, 19.1 ppm;

HRMS (EI$^+$) calc. for $[C_{30}H_{45}O_4]^+$ 469.3318, found 469.3325.



3,12-Dioxoolean-9(11)-en-28,13*β*-olide (10)

Compound **10** was synthesized from **9** (0.5 g, 1.07 mmol) according to the synthetic procedure of **2** (method 2), giving an amorphous solid (0.31 g, 84%), and 0.13 g of **9** was recovered.

m.p.243-245 °C;

$[\alpha]_{D}^{25}$ 66.5 (*c* 1.0, in CH_2Cl_2);

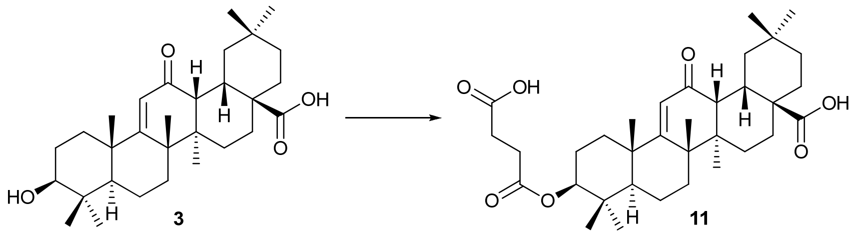
IR (KBr, cm^{-1}): 3457, 2942, 2868, 1785, 1705, 1666, 1590, 1466, 1386, 1357;

ESI-MS: 467 $[M+H]^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 6.03 (s, 1H), 2.99 (m, 1H), 2.66, 2.49, 2.22 (m, each 1H), 1.57, 1.44, 1.38, 1.14, 1.11, 1.00, 0.92 (s, each 3H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 215.3, 192.0, 182.0, 178.4, 122.8, 87.8, 50.9, 47.6, 46.1, 44.0, 43.5, 41.8, 39.8, 37.0, 36.7, 34.1, 33.1, 33.1, 31.6, 29.9, 29.7, 27.2, 26.3, 25.9, 24.3, 23.8, 23.0, 21.6, 21.4, 18.4 ppm;

HRMS (EI^+) calc. for $[C_{30}H_{43}O_4]^+$ 467.3161, found 467.3172.



3β-(3-Carboxy-1-oxopropoxy)-12-oxoolean-9(11)-en-28-oate (11)

To a solution of **3** (2.0 g, 4.26 mmol) and butanedioic anhydride (1.7 g, 17.0 mmol) in anhydrous CH_2Cl_2 (50 mL) was added DMAP (0.51 g, 4.26 mmol). The mixture was refluxed for 12 h, and then was washed with water (50 mL × 3) followed by brine (50 mL × 3), then dried over anhydrous Na_2SO_4. After filtration, the filtrate was evaporated in vacuo, and purified by flash column chromatography (petroleum ether/EtOAc) to afford **11** as an amorphous solid (1.99 g, 82%).

m.p.186-190 °C;

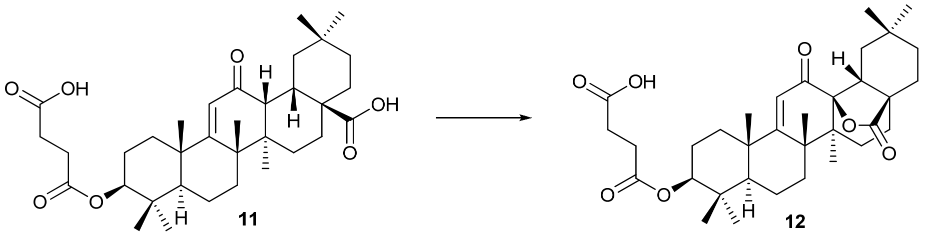
IR (KBr, cm^{-1}): 3458, 2950, 2861, 2648, 2271, 1731, 1659, 1584, 1466, 1384;

ESI-MS: 571 $[M+H]^+$;

^{1}H NMR (300M Hz, DMSO-d_6, 25 °C, TMS): δ 5.75 (s, 1H), 4.54 (m, 1H), 3.01 (m, 1H), 2.91 (d, *J* = 4.5 Hz, 1H), 2.69-2.64 (m, 4H), 1.57, 1.26, 1.61, 1.09, 1.06, 1.00, 0.94 (s, each 3H) ppm;

^{13}C NMR (75M Hz, DMSO-d_6, 25 °C, TMS): δ 199.7, 179.4, 178.4, 173.8, 172.0, 122.4, 79.6, 50.1, 49.2, 46.5, 45.4, 41.7, 39.9, 38.3, 36.1, 35.9, 34.4, 33.6, 33.0, 32.7, 31.6, 30.7 , 29.7, 29.3, 28.1, 28.0, 24.1, 24.0, 23.5, 23.5, 22.8, 21.6, 17.8, 17.1 ppm;

HRMS (EI^+) calc. for $[C_{34}H_{51}O_7]^+$ 571.3635, found 571.3648.



3β-(3-Carboxy-1-oxopropoxy)-12-oxoolean-9(11)-en-28,13*β*-olide (12)

Compound **12** was synthesized from **11** (0.5 g, 0.88 mmol) according to the synthetic procedure of **2** (method 2), giving an amorphous solid (0.36 g, 78%), and 0.04 g of **11** was recovered.

m.p.255-257 °C;

$[\alpha]_D^{25}$ 49.5 (*c* 1.0, in CH_2Cl_2);

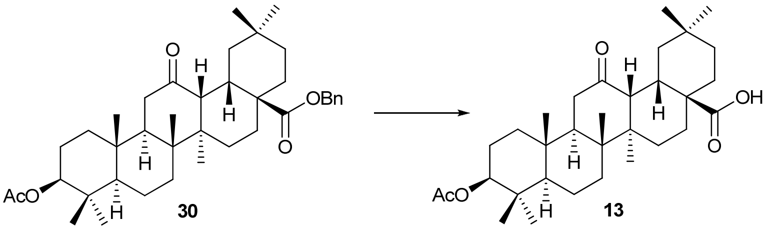
IR (KBr, cm^{-1}): 3449, 2946, 2867, 1766, 1740, 1728, 1674, 1584, 1472, 1387;

ESI-MS: 569 $[M+H]^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 5.90 (s, 1H), 4.55 (m, 1H), 2.98 (m, 1H), 2.70-2.64 (m, 4H), 1.46, 1.28, 1.20, 0.99, 0.97, 0.93, 0.92 (s, each 3H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 192.3, 183.4, 178.7, 177.8, 171.8, 121.7, 87.8, 80.1, 50.4, 46.0, 44.0, 43.6, 41.7, 40.3, 38.3, 36.7, 36.1, 34.1, 33.9, 33.1, 31.6, 30.0, 29.3, 29.0, 27.9, 27.2, 25.8, 24.4, 23.8, 23.7, 23.0, 20.2, 17.1, 16.1 ppm;

HRMS (EI^+) calc. for $[C_{34}H_{49}O_7]^+$ 569.3478, found 569.3466.



3β-Acetoxy-12-oxoolean-28-oate (13)

Compound **13** was synthesized from **30** (2.0 g, 3.58 mmol) according to the synthetic procedure of **3**, giving an amorphous solid (1.68 g, 99%).

m.p.285-287 °C;

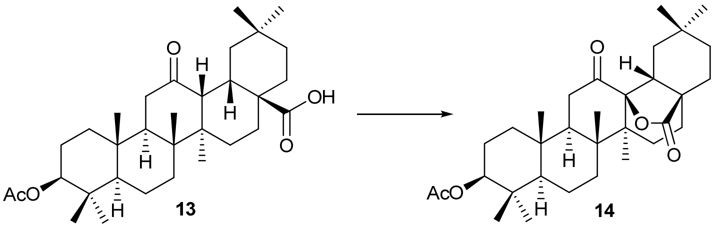
IR (KBr, cm^{-1}): 3448, 2944, 2861, 1731, 1692, 1463, 1451, 1381, 1366, 1249;

ESI-MS: 515 $[M+H]^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 4.50 (m, 1H), 2.92 (m, 1H), 2.69 (d, *J* = 4.5 Hz, 1H), 2.29-2.15 (m, 2H), 2.19 (s, 3H), 0.99, 0.98, 0.95, 0.91, 0.88, 0.87, 0.85 (s, each 3H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 211.3, 183.6, 170.9, 80.4, 55.2, 51.9, 49.7, 47.2, 41.9, 41.4, 38.5, 37.8, 37.7, 36.9, 36.1, 34.5, 33.4, 33.1, 31.9, 31.8, 30.7, 29.7, 27.9, 27.6, 23.4, 23.1, 22.6, 21.3, 20.5, 18.2, 16.4, 15.3 ppm;

HRMS (EI$^+$) calc. for $[C_{32}H_{51}O_5]^+$ 515.3737, found 515.3752.



3β-Acetoxy-12-oxoolean-28,13*β*-olide (14)

Compound **14** was synthesized from **13** (0.5 g, 0.97 mmol) according to the synthetic procedure of **2** (method 2), giving an amorphous solid (0.21 g, 61%), and 0.15 g of **13** was recovered.

m.p.215-216 °C;

$[\alpha]_D^{25}$ 16.7 (*c* 1.0, in CH_2Cl_2);

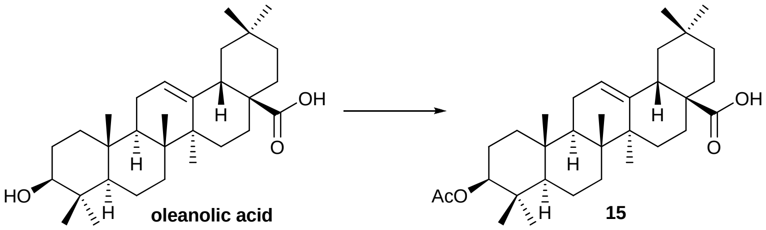
IR (KBr, cm^{-1}): 3506, 2954, 2926, 2855, 2353, 1770, 1729, 1714, 1647, 1590;

ESI-MS: 530 $[M+NH_4]^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 4.50 (m, 1H), 2.76 (t, *J* = 14.4 Hz, 1H), 2.57 (t, *J* = 8.4 Hz, 1H), 2.39 (m, 1H), 2.09 (s, 3H), 1.35, 1.25, 0.97, 0.96, 0.93, 0.87, 0.85 (s, each 3H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 206.0, 178.4, 170.9, 91.0, 80.3, 55.1, 51.1, 44.0, 44.0, 43.7, 42.6, 38.2, 37.9, 37.4, 37.2, 34.2, 33.2, 33.0, 31.6, 29.7, 27.9, 27.3, 25.9, 23.8, 23.4, 21.2, 20.7, 18.5, 18.2, 17.5, 16.4, 15.9 ppm;

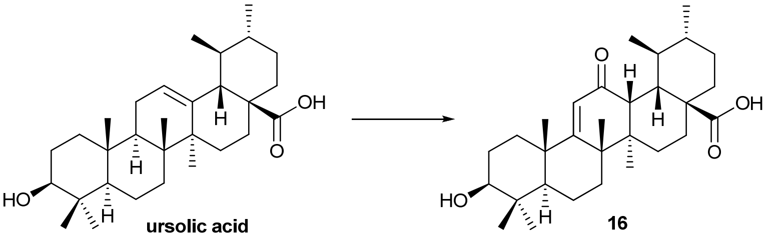
HRMS (EI$^+$) calc. for $[C_{32}H_{48}O_5Na]^+$ 535.3399, found 535.3412.



3β-Acetoxyolean-12-en-28-oate (15)

Compound **15** (CAS 4339-72-4) was prepared from oleanolic acid according to the reported procedure.[3]

m.p.265-267 °C(Lit[4]. 264-265 °C).



3β-Hydroxy-12-oxours-9(11)-en-28-oate (16)

Compound **16** was synthesized from ursolic acid (2.0 g, 4.38 mmol) according to the synthetic procedure of **3**, giving an amorphous solid (0.98 g, 47%).

m.p.242-244 °C;

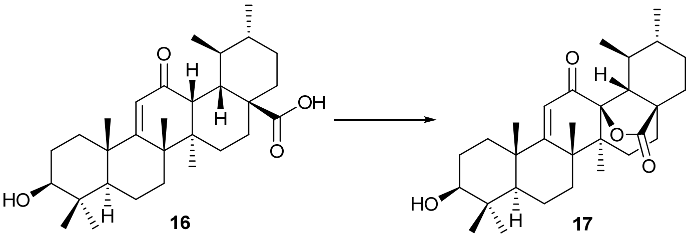
IR (KBr, cm^{-1}): 3630, 3483, 2931, 2872, 1782, 1664, 1458, 1385, 1284, 1240;

ESI-MS: 470 $[M+H]^+$, 493 $[M+Na]^+$;

^{1}H NMR (300M Hz, DMSO-d$_6$, 25 °C, TMS): δ 5.74 (s, 1H), 4.41 (brs, 1H), 3.01 (m, 1H), 2.71-2.67 (d, *J* = 11.0 Hz, 1H), 2.51 (m, 1H), 1.13, 1.09, 1.05, 0.95, 0.86, 0.73 (s, each 3H) ppm;

^{13}C NMR (75M Hz, DMSO-d$_6$, 25 °C, TMS): δ 199.8, 179.8, 179.5, 122.6, 76.6, 50.7, 50.0, 49.2, 45.3, 42.4, 40.8, 40.6, 39.7, 39.3, 39.1, 37.0, 36.4, 32.9, 31.2, 28.7, 28.4, 27.8, 24.8, 24.6, 24.0, 21.0, 20.1, 19.5, 18.0, 16.5 ppm;

HRMS (EI$^+$) calc. for $[C_{30}H_{47}O_4]^+$ 471.3474, found 471.3485.



3β-Hydroxy-12-oxours-9(11)-en-28,13*β*-olide (17)

Compound **17** was synthesized from **16** (0.5 g, 0.97 mmol) according to the synthetic procedure of **2** (method 2), giving an amorphous solid (0.35 g, 85%), and 0.08 g of **16** was recovered.

m.p.256-258 °C;

$[\alpha]_D^{25}$ 51.4 (*c* 1.0, in CH_2Cl_2);

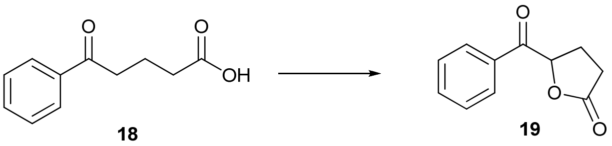
IR (KBr, cm^{-1}): 3488, 3428, 2962, 2937, 2875, 1783, 1769, 1733, 1664, 1632;

ESI-MS: 469 $[M+H]^+$, 491 $[M+Na]^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 6.06 (s, 1H), 3.25 (m, 1H), 2.55 (d, *J* = 11.6 Hz, 1H), 1.49, 1.26, 1.16, 1.05, 0.95, 0.93, 0.85 (s, each 3H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 193.1, 184.6, 178.5, 121.5, 88.0, 77.8, 54.6, 50.2, 45.7, 44.9, 42.4, 40.5, 39.6, 39.3, 37.3, 36.4, 33.9, 31.2, 30.7, 30.3, 28.2, 27.5, 26.1, 24.5, 21.8, 20.4, 19.3, 18.2, 17.3, 15.6 ppm;

HRMS (EI^+) calc. for $[C_{30}H_{45}O_4]^+$ 469.3318, found 469.3328.



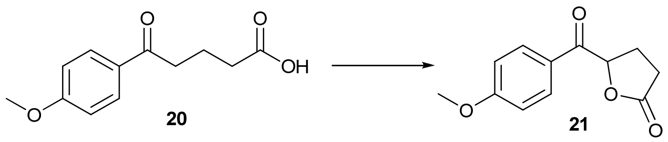
(±)-5-(Phenylcarbonyl)dihydrofuran-2(3H)-one (19)

A mixture of 4-Benzoylbutyric acid (**18**) (0.20 g, 1.0 mmol) and DDQ (0.24 g, 1.0 mmol) in anhydrous benzene (50 mL) was refluxed for 168 h. After filtration, the filtrate was evaporated in vacuo to give a residue, which was purified by flash column chromatography (hexane/ethylether) to give **19** (CAS 35304-85-9) as a light yellow viscous liquid (0.048 g, 54%), and 0.11 g of **18** was recovered.

ESI-MS: 191 $[M+H]^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 7.97-7.16 (m, 5H), 5.88-5.80 (m, 1H), 2.67-2.41 (m, 4H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 194.4, 176.0, 134.3, 134.3, 129.1, 128.8, 78.3, 26.9, 25.0 ppm.



(±)-5-(4-Methoxy-phenylcarbonyl)dihydrofuran-2(3H)-one (21)

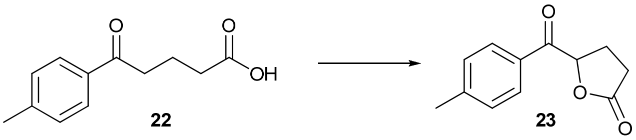
Compound **21** (CAS 24962-85-4) was synthesized from 4-(4-methoxybenzoyl)butyric acid (**20**) (0.20 g, 0.90 mmol) according to the synthetic procedure of **19**, giving an amorphous solid (0.035 g, 51%), and 0.13 g of **20** was recovered.

m.p.125-126 °C;

ESI-MS: 221 $[M+H]^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 7.99-6.97 (m, 4H), 5.76-5.71 (m, 1H), 3.89 (s, 3H), 2.67-2.46 (m, 4H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 192.6, 176.3, 164.4, 131.1, 131.1, 126.7, 114.3, 114.3, 78.1, 55.6, 26.9, 25.0 ppm.



(±)-5-(4-Methyl-phenylcarbonyl)dihydrofuran-2(3H)-one (23)

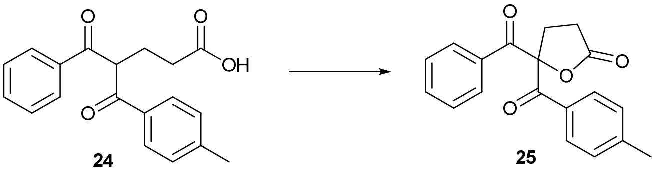
Compound **23** (CAS 420119-86-4) was synthesized from 4-(4-methoxybenzoyl)butyric acid (**22**) (0.20 g, 0.97 mmol) according to the synthetic procedure of **19**, giving an amorphous solid (0.052 g, 58%), and 0.11 g of **22** was recovered.

m.p.84-86 °C;

ESI-MS: 205 $[M+H]^+$;

^{1}HNMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 7.89-7.26 (m, 4H), 5.79-5.74 (m, 1H), 2.65-2.39 (m, 7H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 193.9, 175.2, 145.4, 131.2, 129.7, 129.7, 128.9, 128.9, 78.2, 29.7, 25.0, 21.7 ppm.



(±)-5-(4-Methyl-phenylcarbonyl)-5-phenylcarbonyl-dihydrofuran-2(3H)-one (25)

Compound **25** was synthesized from 4-(4-methylbenzoyl)-4-benzoylbutyric acid (**24**) (0.2 g, 0.65 mmol) according to the synthetic procedure of **19**, giving an viscous liquid (0.039 g, 36%), and 0.09 g of **24** was recovered.

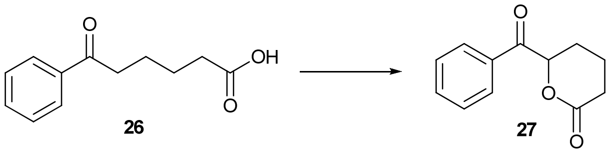
ESI-MS: 309 $[M+H]^+$;

IR (KBr, cm^{-1}): 3445, 3061, 2908, 2235, 1702, 1677, 1605, 1554, 1448, 1413;

^{1}HNMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 7.59-6.90 (m, 9H), 3.06-2.04 (m, 7H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 195.8, 195.4, 177.6, 144.7, 135.8, 133.6, 133.6, 133.3, 129.6, 129.6, 128.9, 128.9, 128.8, 128.8, 128.6, 128.6, 55.0, 31.1, 23.9 ppm.

HRMS (EI$^+$) calc. for $[C_{19}H_{16}O_4K]^+$ 347.0686, found 347.0690.



(±)-6-Benzoyltetrahydro-2*H*-pyran-2-one (27)

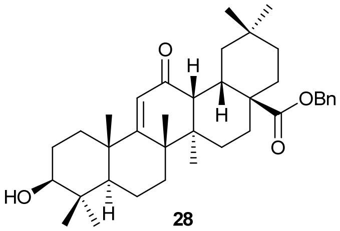
Compound **27** (CAS 184171-69-5) was synthesized from benzenehexanoic acid (**26**) (0.2 g, 0.97 mmol) according to the synthetic procedure of **19**, giving an amorphous solid (0.074 g, 62%), and 0.08 g of **26** was recovered.

m.p.121-123 °C;

ESI-MS: 205 [M+H]$^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 7.96-7.47 (m, 5H), 5.13-5.08 (m, 1H), 3.65-3.20 (m, 2H), 2.65-2.57 (m, 3H), 2.09-1.97 (m, 1H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 196.2, 176.6, 136.4, 133.7, 128.8, 128.8, 128.0, 128.0, 76.5, 43.8, 28.5, 28.3 ppm.



Benzyl 3β-hydroxy-12-oxoolean-9(11)-en-28-oate (28)

Compound **28** was synthesized according to literature[1].

m.p. 197-198 °C;

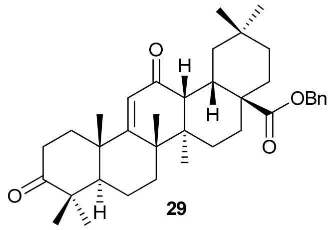
IR (KBr, cm^{-1}): 3506, 2953, 2930, 2867, 1715, 1647, 1587, 1456, 1382, 1236;

ESI-MS: 561 [M+H]$^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 7.34-7.29 (m, 5H), 5.7 (s, 1H), 5.18 (d, J = 12.6 Hz, 1H), 5.13 (d, J = 12.6 Hz, 1H), 3.22-3.17 (m, 1H), 3.08 (m, 1H), 2.75 (d, J = 4.2 Hz, 1H), 1.14, 1.02, 1.00, 0.96, 0.92, 0.89, 0.81 (s, each 3H) ppm;

^{13}C NMR (75M Hz, CDCl$_3$, 25 °C, TMS): δ 200.4, 178.5, 177.5, 136.3, 128.5, 128.5, 128.4, 128.4, 128.1, 122.6, 77.8, 66.1, 50.2, 49.3, 47.2, 45.3, 41.7, 40.0, 39.3, 36.5, 35.9, 34.5, 33.3, 32.9, 32.8, 31.6, 30.7, 28.1, 28.0, 27.5, 23.8, 23.4, 23.2, 22.8, 21.7, 18.0, 15.7 ppm;

HRMS (EI$^+$) calc. for $[C_{37}H_{53}O_4]^+$ 561.3944, found 561.3968.



29

Benzyl 3,12-dioxoolean-9(11)-en-28-oate (29)

Compound **29** was synthesized according to literature[1].

m.p. 146-147 °C;

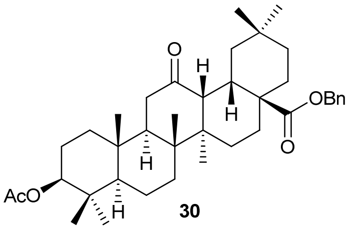
IR (KBr, cm^{-1}): 3421, 2946, 2861, 2359, 1723, 1708, 1662, 1599, 1466, 1383;

ESI-MS: 559 $[M+H]^+$;

^{1}H NMR (300M Hz, CDCl$_3$, 25 °C, TMS): δ 7.38-7.28 (m, 5H), 5.8 (s, 1H), 5.19 (d, *J* = 12.6 Hz, 1 H), 5.14 (d, *J* = 12.6 Hz, 1H), 3.09 (m, 1H), 2.79 (d, *J* = 4.5 Hz, 1H), 2.66, 2.49, 2.17 (m, each 1H), 1.26, 1.11, 1.07, 1.00, 0.97, 0.95, 0.89 (s, each 3H) ppm;

^{13}C NMR (75M Hz, CDCl$_3$, 25 °C, TMS): δ 215.7, 199.9, 177.4, 176.6, 136.3, 128.5, 128.5, 128.4, 128.4, 128.2, 124.0, 50.9, 49.5, 47.5, 47.2, 45.4, 41.8, 39.4, 37.0, 35.9, 34.5, 34.2, 33.3, 32.8, 31.9, 31.6, 30.7, 29.7, 28.0, 26.3, 23.8, 23.3, 23.2, 22.8, 21.6, 21.4, 19.1 ppm;

HRMS (EI$^+$) calc. for $[C_{37}H_{50}O_4Na]^+$ 581.3607, found 581.3625.



30

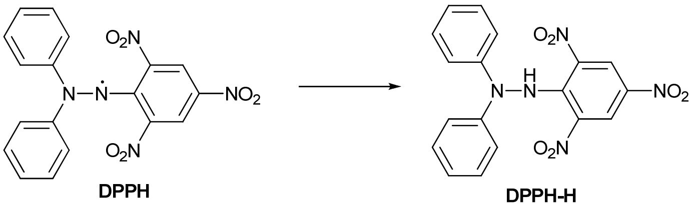
Benzyl 3β-acetoxy-12-oxoolean-28-oate (30)

Compound **30** (CAS 357953-28-7) was synthesized according to literature[1].

m.p. 196-198 °C;

ESI-MS: 605 $[M+H]^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 7.34-7.31 (m, 5H), 5.21 (d, *J* = 12.2 Hz, 1H), 5.13 (d, *J* = 12.2 Hz, 1H), 4.46 (m, 1H), 2.83 (m, 1H), 2.43 (d, *J* = 4.1 Hz, 1H), 1.99, 1.03, 0.99, 0.92, 0.90, 0.85, 0.81 (s, each 3H) ppm;



2,2-Diphenyl-1-picrylhydrazine (DPPH-H)

A mixture of CDDO (0.25 g, 0.51 mmol) and DPPH• (0.40 g, 1.02 mmol) in anhydrous benzene (30 mL) was refluxed for 48 h. After filtration, the filtrate was evaporated in vacuo to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc) to give DPPH-H (CAS 1707-75-1) as a purple-black solid (0.20g, 80.3%).

m.p. 176-178 °C;

IR (KBr, cm^{-1}): 3510, 3422, 3264, 3121, 3062, 2920, 1624, 1597, 1538, 1505;

ESI-MS: 394 $[M-H]^-$;

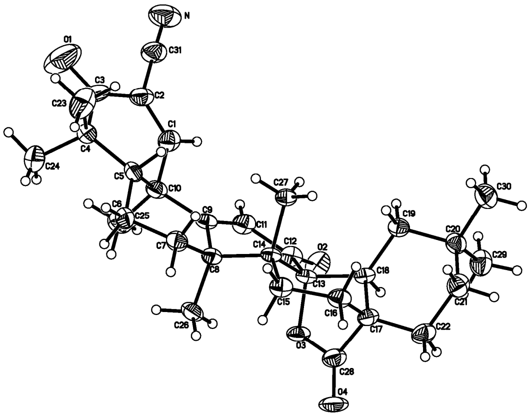
^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 10.1(s, 1H), 9.21 (s, 1H), 8.51(s, 1H), 7.53-7.01(m, 10H) ppm;

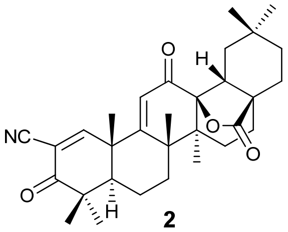
^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 146.0, 146.0, 142.0, 142.0, 136.4, 129.5, 129.5, 129.5, 129.5, 126.2, 125.8, 125.8, 125.8, 124.9, 120.4, 120.4, 120.4, 120.4 ppm;

HRMS (EI^+) calc. for $[C_{18}H_{12}N_5O_6]^-$ 394.0801, found 394.0796.

3. Crystallographic data of compound 2

CCDC 793908 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.





2

Table.1a Crystal data and structure refinement for 2.

Bone precision	0.0067 Å
Wavelength	0.71073
Cell	a = 8.9020(18)Å α = 90°
	b = 12.345 (3)Å β = 90°
	c = 24.222 (5)Å γ = 90°
Temperature	293K
Volume	2661.9
Space group	P212121
Hall group	P2ac2ab
Formual	$C_{31}H_{39}NO_4$
Mr	489.63
Dx, gcm^{-3}	1.222
Z	4
Mu (mm^{-1})	0.080
F000	1056.0
F000’	1056.46
H, k, lmax	10, 14, 29
Nref	2763 [4844]
Tmin, Tmax	0.981, 0.992
Tmin’	0.976

Correction method	PSI-SCAN
Data completeness	1.74/1.00
Theta (max)	25.290
R (reflections)	0.0702 (3079)
wR2 (reflections)	0.1942 (4821)
S	1.007
Npar	326

Table 1b. Atomic coordinates and equivalent isotropic displacement parameters for 2.

	x	y	z	U(eq)
C1	1.0088(6)	-0.0786(4)	-0.05234(18)	0.0529(13)
O1	1.2810(7)	-0.2114(5)	-0.1352(3)	0.147(3)
O2	0.6598(4)	0.1210(3)	0.07556(15)	0.0650(10)
O3	0.8857(4)	0.2317(2)	0.14122(12)	0.0483(8)
O4	0.8964(6)	0.3456(3)	0.21336(15)	0.0805(13)
N	0.9100(7)	-0.3082(4)	-0.1257(2)	0.0941(18)
C2	1.0726(6)	-0.1571(4)	-0.0823(2)	0.0539(13)
C3	1.2348(8)	-0.1580(4)	0.0947(3)	0.0763(18)
C4	1.3412(6)	-0.0903(4)	-0.0610(2)	0.0539(13)
C5	1.2581(5)	-0.0344(4)	-0.01288(18)	0.0473(12)
C6	1.3496(6)	0.0485(4)	0.0181(2)	0.0571(12)
C7	1.2819(5)	0.0675(4)	0.0749(2)	0.0509(12)
C8	1.1171(5)	0.1013(3)	0.07410(17)	0.0398(10)
C9	1.0248(5)	0.0518 (3)	0.02695 (18)	0.0400(10)
C10	1.1008(6)	0.0117(3)	-0.02643(18)	0.0464(11)
C11	0.8741(6)	0.0559(4)	0.03123(18)	0.0503(12)
C12	0.7909(6)	0.0992(4)	0.0791(2)	0.0457(11)
C13	0.8775(5)	0.1126(3)	0.13337(17)	0.0367(9)
C14	1.0373(5)	0.0677(3)	0.13003(17)	0.0356 (9)

C15	1.1240(5)	0.1086(4)	0.18094(18)	0.0492(12)
C16	1.0296(5)	0.1035(4)	0.23416(18)	0.0485(12)
C17	0.8712(5)	0.1479(3)	0.22810(18)	0.0437(11)
C18	0.7853(5)	0.0832(3)	0.18420(17)	0.0370(10)
C19	0.7432(5)	-0.0315(3)	0.20339(19)	0.0453(11)
C20	0.6481(5)	-0.0261(4)	0.2566(2)	0.0497(12)
C21	0.7375(6)	0.0401(4)	0.3005(2)	0.0595(13)
C22	0.7832(6)	0.1548(4)	0.2811(2)	0.0572(14)
C23	1.4574(7)	-0.1688(6)	-0.0380(3)	0.094(2)
C24	1.4213(9)	-0.0144 (5)	-0.1003 (3)	0.104(3)
C25	1.0974(7)	0.1068(4)	-0.0689(2)	0.0685(16)
C26	1.1192(6)	0.2265(3)	0.06348(19)	0.0583(13)
C27	1.0303(5)	-0.0587(3)	0.13191(19)	0.0419(10)
C28	0.8834(6)	0.2541(4)	0.19692(19)	0.0557(12)
C30	0.6275(7)	-0.1408(4)	0.2781(2)	0.0705(16)
C29	0.4914(6)	0.0221(5)	0.2462(3)	0.0688(15)
C31	0.9836(7)	-0.2403(4)	-0.1068(2)	0.0662(15)

Table 1c. Hydrogen coordinates and isotropic displacement parameters for 2.

	x	y	z	U(eq)
H1A	0.9053	-0.0794	-0.0472	0.063
H5A	1.2394	-0.0923	0.0139	0.057
H6A	1.3514	0.1160	-0.0023	0.068
H6B	1.4522	0.0231	0.0220	0.068
H7A	1.3395	0.1233	0.0935	0.061
H7B	1.2913	0.0015	0.0963	0.061
H11A	0.8181	0.0294	0.0017	0.060
H15A	1.1552	0.1828	0.1746	0.059
H15B	1.2137	0.0650	0.1857	0.059

H16A	1.0235	0.0287	0.2462	0.058
H16B	1.0810	0.1440	0.2628	0.058
H18A	0.6896	0.1215	0.1796	0.044
H19A	0.8327	-0.0733	0.2101	0.054
H19B	0.6852	-0.0674	0.1746	0.054
H21A	0.6765	0.0466	0.3335	0.071
H21B	0.8275	0.0002	0.3103	0.071
H22A	0.6939	0.1984	0.2753	0.069
H22B	0.8437	0.1895	0.3093	0.069
H23A	1.4091	-0.2192	-0.0136	0.141
H23B	1.5325	-0.1291	-0.0180	0.141
H23C	1.5039	-0.2074	-0.0678	0.141
H24A	1.3514	0.0379	-0.1143	0.156
H24B	1.4628	-0.0553	-0.1304	0.156
H24C	1.5008	0.0222	-0.0810	0.156
H25A	1.1437	0.0840	-0.1028	0.103
H25B	1.1513	0.1677	-0.0542	0.103
H25C	0.9952	0.1274	-0.0759	0.103
H26A	1.1681	0.2411	0.0289	0.087
H26B	1.1728	0.2619	0.0928	0.087
H26C	1.0180	0.2533	0.0622	0.087
H27A	1.0363	-0.0827	0.1696	0.063
H27B	1.1129	-0.0882	0.1114	0.063
H27C	0.9374	-0.0829	0.1160	0.063
H30A	0.5733	-0.1829	0.2514	0.106
H30B	0.5721	-0.1389	0.3121	0.106
H30C	0.7241	-0.1731	0.2844	0.106
H29A	0.4409	-0.0196	0.2183	0.103
H29B	0.5014	0.0957	0.2339	0.103

H29C	0.4342	0.0202	0.2798	0.103

Table 1d. Anisotropic displacement parameters for 2.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	0.066(3)	0.053(3)	0.039(3)	-0.001(2)	-0.004(2)	0.002(2)
O1	0.131(4)	0.149(5)	0.160(5)	-0.096(5)	0.014(4)	-0.002(4)
O2	0.051(2)	0.089(3)	0.055(2)	-0.0049(19)	-0.0116(18)	0.0141(18)
O3	0.071(2)	0.0238(14)	0.0498(19)	-0.0001(13)	-0.0044(17)	0.0084(14)
O4	0.142(4)	0.0321(18)	0.067(2)	-0.0180(17)	0.003(2)	-0.004(2)
N	0.140(5)	0.064(3)	0.078(4)	-0.012(3)	-0.020(4)	-0.019(3)
C2	0.079(4)	0.039(2)	0.044(3)	-0.004(2)	-0.007(3)	-0.002(2)
C3	0.097(5)	0.049(3)	0.083(4)	-0.031(3)	0.002(4)	0.007(3)
C4	0.069(3)	0.042(3)	0.051(3)	0.001(2)	0.014(3)	-0.003(2)
C5	0.054(3)	0.042(3)	0.046(2)	0.005(2)	0.008(2)	-0.013(2)
C6	0.054(3)	0.058(3)	0.059(3)	-0.008(2)	0.014(2)	-0.015(3)
C7	0.049(3)	0.051(3)	0.053(3)	-0.008(2)	-0.003(2)	-0.014(2)
C8	0.044(3)	0.033(2)	0.042(2)	-0.0033(19)	-0.005(2)	-0.006(2)
C9	0.052(3)	0.025(2)	0.043(2)	0.0030(18)	-0.009(2)	0.0008(19)
C10	0.065(3)	0.034(2)	0.040(3)	0.0027(19)	-0.004(2)	-0.005(2)
C11	0.063(3)	0.050(3)	0.037(3)	-0.005(2)	-0.014(2)	-0.004(3)
C12	0.049(3)	0.043(3)	0.045(3)	0.002(2)	-0.011(2)	0.001(2)
C10	0.065(3)	0.034(2)	0.040(3)	0.0027(19)	-0.004(2)	-0.005(2)
C11	0.063(3)	0.050(3)	0.037(3)	-0.005(2)	-0.014(2)	-0.004(3)
C12	0.049(3)	0.043(3)	0.045(3)	0.002(2)	-0.011(2)	0.001(2)
C13	0.049(3)	0.0211(18)	0.040(2)	-0.0021(17)	-0.010(2)	-0.0008(19)
C14	0.042(2)	0.0251(19)	0.040(2)	-0.0043(17)	-0.010(2)	-0.0037(18)
C15	0.053(3)	0.046(3)	0.048(3)	-0.002(2)	-0.011(2)	0.001(2)
C16	0.059(3)	0.044(3)	0.042(3)	-0.006(2)	-0.014(2)	-0.005(2)
C17	0.056(3)	0.034(2)	0.041(3)	-0.0047(19)	-0.001(2)	0.006(2)

C18	0.043(2)	0.029(2)	0.038(2)	-0.0052(18)	-0.006(2)	0.0056(19)
C19	0.048(3)	0.037(2)	0.051(3)	0.002(2)	-0.003(2)	0.005(2)
C20	0.049(3)	0.044(3)	0.056(3)	0.008(2)	0.002(2)	0.003(2)
C21	0.068(3)	0.060(3)	0.050(3)	0.005(2)	0.001(2)	0.003(2)
C22	0.073(4)	0.055(3)	0.043(3)	-0.013(2)	-0.006(2)	0.002(3)
C23	0.085(4)	0.115(6)	0.082(4)	-0.002(4)	0.013(4)	0.028(4)
C24	0.144(7)	0.079(4)	0.090(5)	-0.002(4)	0.067(5)	-0.009(4)
C25	0.103(4)	0.049(3)	0.053(3)	0.011(3)	0.004(3)	-0.005(3)
C26	0.085(4)	0.039(2)	0.052(3)	0.003(2)	0.005(3)	-0.018(3)
C27	0.047(2)	0.031(2)	0.048(3)	0.001(2)	-0.005(2)	-0.006(2)
C28	0.076(3)	0.043(3)	0.048(3)	-0.009(2)	-0.003(3)	0.002(3)
C30	0.079(4)	0.061(3)	0.072(4)	0.015(3)	0.013(3)	0.000(3)
C29	0.059(3)	0.077(4)	0.071(3)	0.002(3)	0.010(3)	0.002(3)
C31	0.097(4)	0.054(3)	0.048(3)	-0.008(3)	-0.005(3)	-0.006(3)

Table 1e. Bond lengths [Å] for 2.

C1-C2	1.336(7)	C16-C17	1.520(6)
C1-C10	1.520(6)	C16-H16A	0.9700
C1- H1A	0.9300	C16-H16B	0.9700
O1-C3	1.252(7)	C17-C22	1.506(6)
O2-C12	1.201(5)	C17-C28	1.517(6)
O3-C28	1.378(5)	C17-C18	1.534(6)
O3-C13	1.485(4)	C18-C19	1.539(6)
O4-C28	1.202(5)	C18-H18A	0.9800
N-C31	1.158(7)	C19-C20	1.539(7)
C2-C31	1.427(7)	C19-H19A	0.9700
C2-C3	1.475(8)	C19-H19B	0.9700
C3-C4	1.503(8)	C20-C30	1.520(7)
C4-C24	1.514(7)	C20-C29	1.537(7)

C4-C23	1.523(8)	C20-C21	1.559(7)
C4-C5	1.543(6)	C21-C22	1.547(7)
C5-C6	1.508(6)	C21-H21A	0.9700
C5-C10	1.547(7)	C21-H21B	0.9700
C5-H5A	0.9800	C22-H22A	0.9700
C6-C7	1.520(6)	C22-H22B	0.9700
C6-H6A	0.9700	C23-H23A	0.9600
C6-H6B	0.9700	C23-H23B	0.9600
C7-C8	1.525(6)	C23-H23C	0.9600
C7-H7A	0.9700	C24-H24A	0.9600
C7-H7B	0.9700	C24-H24B	0.9600
C8-C9	1.534(6)	C24-H24C	0.9600
C8-C26	1.567(6)	C25-H25A	0.9600
C8-C14	1.585(6)	C25-H25B	0.9600
C9-C11	1.346(7)	C25-H25C	0.9600
C9-C10	1.541(6)	C26-H26A	0.9600
C10-C25	1.562(6)	C26-H26B	0.9600
C11-C12	1.475(7)	C26-H26C	0.9600
C11-H11A	0.9300	C27-H27A	0.9600
C12-C13	1.534(6)	C27-H27B	0.9600
C13-C18	1.524(6)	C27-H27C	0.9600
C13-C14	1.529(6)	C30-H30A	0.9600
C14-C15	1.540(6)	C30-H30B	0.9600
C14-C27	1.562(5)	C30-H30C	0.9600
C15-C16	1.540(6)	C29-H29A	0.9600
C15-H15A	0.9700	C29-H29B	0.9600
C15-H15B	0.9700	C29-H29C	0.9600

Table 1f. Bond angles [°] for 2.

C2-C1-C10	121.8(5)	C28-C17-C16	107.1(4)
C2-C1-H1A	119.1	C22-C17-C18	111.1(4)
C10-C1-H1A	119.1	C28-C17-C18	98.1(3)
C28-O3-C13	108.9(3)	C16-C17-C18	110.0(3)
C1-C2-C31	120.8(5)	C13-C18-C17	99.7(3)
C1-C2-C3	122.1(5)	C13-C18-C19	126.6(3)
C31-C2-C3	117.0(5)	C17-C18-C19	113.2(4)
O1-C3-C2	119.0(6)	C13-C18-H18A	105.2
O1-C3-C4	120.8(6)	C17-C18-H18A	105.2
C2-C3-C4	120.1(5)	C19-C18-H18A	105.2
C3-C4-C24	107.4(5)	C18-C19-C20	110.4(3)
C3-C4-C23	105.9(5)	C18-C19-H19A	109.6
C24-C4-C23	107.6(5)	C20-C19-H19A	109.6
C3-C4-C5	110.9(4)	C18-C19-H19B	109.6
C24-C4-C5	115.1(4)	C20-C19-H19B	109.6
C23-C4-C5	109.5 (4)	H19A-C19-H19B	108.1
C6-C5-C4	114.9(4)	C30-C20-C29	107.9(4)
C6-C5-C10	110.2(4)	C30-C20-C19	108.2(4)
C4-C5-C10	116.0(4)	C29-C20-C19	111.9(4)
C6-C5-H5A	104.8	C30-C20-C21	108.4(4)
C4-C5-H5A	104.8	C29-C20-C21	111.8(4)
C10-C5-H5A	104.8	C19-C20-C21	108.4(4)
C5-C6-C7	109.9(4)	C22-C21-C20	114.0(4)
C5-C6-H6A	109.7	C22-C21-H21A	108.8
C7-C6-H6A	109.7	C20-C21-H21A	108.8
C5-C6-H6B	109.7	C22-C21-H21B	108.8
C7-C6-H6B	109.7	C20-C21-H21B	108.8
H6A-C6-H6B	108.2	H21A-C21-H21B	107.7
C6-C7-C8	114.4(4)	C17-C22-C21	110.2(4)

C6-C7-H7A	108.7	C17-C22-H22A	109.6
C8-C7-H7A	108.7	C21-C22-H22A	109.6
C6-C7-H7B	108.7	C17-C22-H22B	109.6
C8-C7-H7B	108.7	C21-C22-H22B	109.6
H7A-C7-H7B	107.6	H22A-C22-H22B	108.1
C7-C8-C9	114.6(4)	C4-C23-H23A	109.5
C7-C8-C26	105.1(4)	C4-C23-H23B	109.5
C9-C8-C26	106.1(4)	H23A-C23-H23B	109.5
C7-C8-C14	110.4(4)	C4-C23-H23C	109.5
C9-C8-C14	107.0(3)	H23A-C23-H23C	109.5
C26-C8-C14	113.8(3)	H23B-C23-H23C	109.5
C11-C9-C8	117.5(4)	C4-C24-H24A	109.5
C11-C9-C10	121.0(4)	C4-C24-H24B	109.5
C8-C9-C10	121.1(4)	H24A-C24-H24B	109.5
C1-C10-C9	110.2(4)	C4-C24-H24C	109.5
C1-C10-C5	107.8(4)	H24A-C24-H24C	109.5
C9-C10-C5	109.7(4)	H24B-C24-H24C	109.5
C1-C10-C25	105.6(4)	C10-C25-H25A	109.5
C9-C10-C25	107.7(4)	C10-C25-H25B	109.5
C5-C10-C25	115.7(4)	H25A-C25-H25B	109.5
C9-C11-C12	125.0(4)	C10-C25-H25C	109.5
C9-C11-H11A	117.5	H25A-C25-H25C	109.5
C12-C11-H11A	117.5	H25B-C25-H25C	109.5
O2-C12-C11	120.9(4)	C8-C26-H26A	110.3(3)
O2-C12-C13	121.7(5)	C8-C26-H26B	109.6
C11-C12-C13	117.4(4)	H26A-C26-H26B	109.6
O3-C13-C18	99.1(3)	C8-C26-H26C	109.5
O3-C13-C14	108.7(3)	H26A-C26-H26C	109.5
C18-C13-C14	117.3(3)	H26B-C26-H26C	109.5

O3-C13-C12	104.0(3)	C14-C27-H27A	109.5
C18-C13-C12	113.4(4)	C14-C27-H27B	109.5
C14-C13-C12	112.5(4)	H27A-C27-H27B	109.5
C13-C14-C15	107.8(3)	C14-C27-H27C	109.5
C13-C14-C27	108.9(3)	H27A-C27-H27C	109.5
C15-C14-C27	108.9(3)	H27B-C27-H27C	109.5
C13-C14-C8	111.5(3)	O4-C28-O3	120.8(4)
C15-C14-C8	112.0(3)	O4-C28-C17	130.8(4)
C27-C14-C8	107.7(3)	O3-C28-C17	108.3(3)
C14-C15-C16	112.6(4)	C20-C30-H30A	109.5
C14-C15-H15A	109.1	C20-C30-H30B	109.5
C16-C15-H15A	109.1	H30A-C30-H30B	109.5
C14-C15-H15B	109.1	C20-C30-H30C	109.5
C16-C15-H15B	109.1	H30A-C30-H30C	109.5
H15A-C15-H15B	107.8	H30B-C30-H30C	109.5
C17-C16-C15	114.2(4)	C20-C29-H29A	109.5
C17-C16-H16A	108.7	C20-C29-H29B	109.5
C15-C16-H16A	108.7	H29A-C29-H29B	109.5
C17-C16-H16B	108.7	C20-C29-H29C	109.5
C15-C16-H16B	108.7	H29A-C29-H29C	109.5
H16A-C16-H16B	107.6	H29B-C29-H29C	109.5
C22-C17-C28	114.4(4)	H29B-C29-H29C	109.5
C22-C17-C16	114.9(4)	N-C31-C2	178.6(6)

Table 1g. Torsion angles [°] for 2.

C10-C1-C2-C31	-179.2(4)	C18-C13-C14-C15	-58.8(4)
C10-C1-C2-C3	-3.4(8)	C12-C13-C14-C15	167.1(3)
C1-C2-C3-O1	-158.4(6)	O3-C13-C14-C27	170.4(3)
C31-C2-C3-O1	17.5(9)	C18-C13-C14-C27	59.2(4)

C1-C2-C3-C4	18.0(8)	C12-C13-C14-C27	-75.0(4)
C31-C2-C3-C4	-166.0(5)	O3-C13-C14-C8	-70.8(4)
O1-C3-C4-C24	54.6(8)	C18-C13-C14-C8	178.0(3)
C2-C3-C4-C24	-121.8(6)	C12-C13-C14-C8	43.8(4)
O1-C3-C4-C23	-60.2(8)	C7-C8-C14-C13	173.1(3)
C2-C3-C4-C23	123.4(6)	C9-C8-C14-C13	-61.7(4)
O1-C3-C4-C5	-178.9(6)	C26-C8-C14-C13	55.2(4)
C2-C3-C4-C5	4.7(7)	C7-C8-C14-C15	52.2(4)
C3-C4-C5-C6	-171.1(4)	C9-C8-C14-C15	177.5(4)
C24-C4-C5-C6	-48.9(7)	C26-C8-C14-C15	-65.7(5)
C23-C4-C5-C6	72.4(6)	C7-C8-C14-C27	-67.5
C3-C4-C5-C10	-40.7(6)	C9-C8-C14-C27	57.7(4)
C24-C4-C5-C10	81.5(6)	C26-C8-C14-C27	174.6(4)
C23-C4-C5-C10	-157.1(4)	C13-C14-C15-C16	41.9(5)
C4-C5-C6-C7	-159.5(4)	C27-C14-C15-C16	-76.0(5)
C10-C5-C6-C7	67.2(5)	C8-C14-C15-C16	164.9(4)
C5-C6-C7-C8	-55.8(6)	C14-C15-C16-C17	-46.3(5)
C6-C7-C8-C9	33.1(5)	C15-C16-C17-C22	-173.7(4)
C6-C7-C8-C26	-82.9(5)	C15-C16-C17-C28	-45.5(5)
C6-C7-C8-C14	153.9(4)	C15-C16-C17-C18	60.1(5)
C7-C8-C9-C11	164.0(4)	O3-C13-C18-C17	-47.7(4)
C26-C8-C9-C11	-80.5(5)	C14-C13-C18-C17	68.9(4)
C14-C8-C9-C11	41.3(5)	C12-C13-C18-C17	-157.3(3)
C7-C8-C9-C10	-23.3(5)	O3-C13-C18-C19	-176.3(4)
C26-C8-C9-C10	92.1(4)	C14-C13-C18-C19	-59.7(5)
C14-C8-C9-C10	-146.0(4)	C12-C13-C18-C19	74.1(5)
C2-C1-C10-C9	-150.3(4)	C22-C17-C18-C13	166.8(3)
C2-C1-C10-C5	-30.5(6)	C28-C17-C18-C13	46.7(4)
C2-C1-C10-C25	93.7(5)	C16-C17-C18-C13	-64.9(4)

C11-C9-C10-C1	-35.5(6)	C22-C17-C18-C19	-56.2(5)
C8-C9-C10-C1	152.1(4)	C28-C17-C18-C19	-176.4(4)
C11-C9-C10-C5	-154.0(4)	C16-C17-C18-C19	72.1(5)
C8-C9-C10-C5	33.6(5)	C13-C18-C19-C20	-179.9(4)
C11-C9-C10-C25	79.2(5)	C17-C18-C19-C20	57.1(5)
C8-C9-C10-C25	-93.1(5)	C18-C19-C20-C30	-172.2(4)
C6-C5-C10-C1	-174.4(4)	C18-C19-C20-C29	69.1(5)
C4-C5-C10-C1	52.9(5)	C18-C19-C20-C21	-54.8(5)
C6-C5-C10-C9	-54.4(5)	C30-C20-C21-C22	173.1(4)
C4-C5-C10-C9	173.0(4)	C29-C20-C21-C22	-68.1(6)
C6-C5-C10-C25	67.7(5)	C19-C20-C21-C22	55.8(5)
C4-C5-C10-C25	-65.0(5)	C28-C17-C22-C21	163.4(4)
C8-C9-C11-C12	-3.4(7)	C16-C17-C22-C21	-72.2(5)
C10-C9-C11-C12	-176.0(4)	C18-C17-C22-C21	53.5(5)
C9-C11-C12-O2	164.3(5)	C20-C21-C22-C17	-55.5(6)
C9-C11-C12-C13	-17.0(7)	C13-O3-C28-O4	176.3(5)
C28-O3-C13-C18	30.8(4)	C13-O3-C28-C17	-0.8(5)
C28-O3-C13-C14	-92.2(4)	C22-C17-C28-O4	36.4(8)
C28-O3-C13-C12	147.7(4)	C16-C17-C28-O4	-92.1(7)
O2-C12-C13-O3	-69.3(6)	C18-C17-C28-O4	154.1(6)
C11-C12-C13-O3	112.1(4)	C22-C17-C28-O3	-146.8(4)
O2-C12-C13-C18	37.3(6)	C16-C17-C28-O3	84.7(5)
C11-C12-C13-C18	-141.4(4)	C18-C17-C28-O3	-29.2(5)
O2-C12-C13-C14	173.3(4)	C1-C2-C31-N	-49(28)
C11-C12-C13-C14	-5.4(5)	C3-C2-C31-N	135(28)
O3-C13-C14-C15	52.5(4)		

4. ESR spectra

ESR measurements: ESR spectra were recorded on Bruker EMX 10/12 ESR SPECTROMETER. Typical spectrometer parameters include: range: 200 G; field set: 3475 G; modulation frequency 100 K

Hz; modulation amplitude: 0.5 G; receiver gain: 5.02e × 10^4; microwave power: 20 mW. *N*-tert-butyl-*α*-phenyl nitrone (PBN) (98%) was purchased from J&K CHEMICA and benzene (GC) was from TOKYO CHEMICAL INDUSTRY CO. LTD.

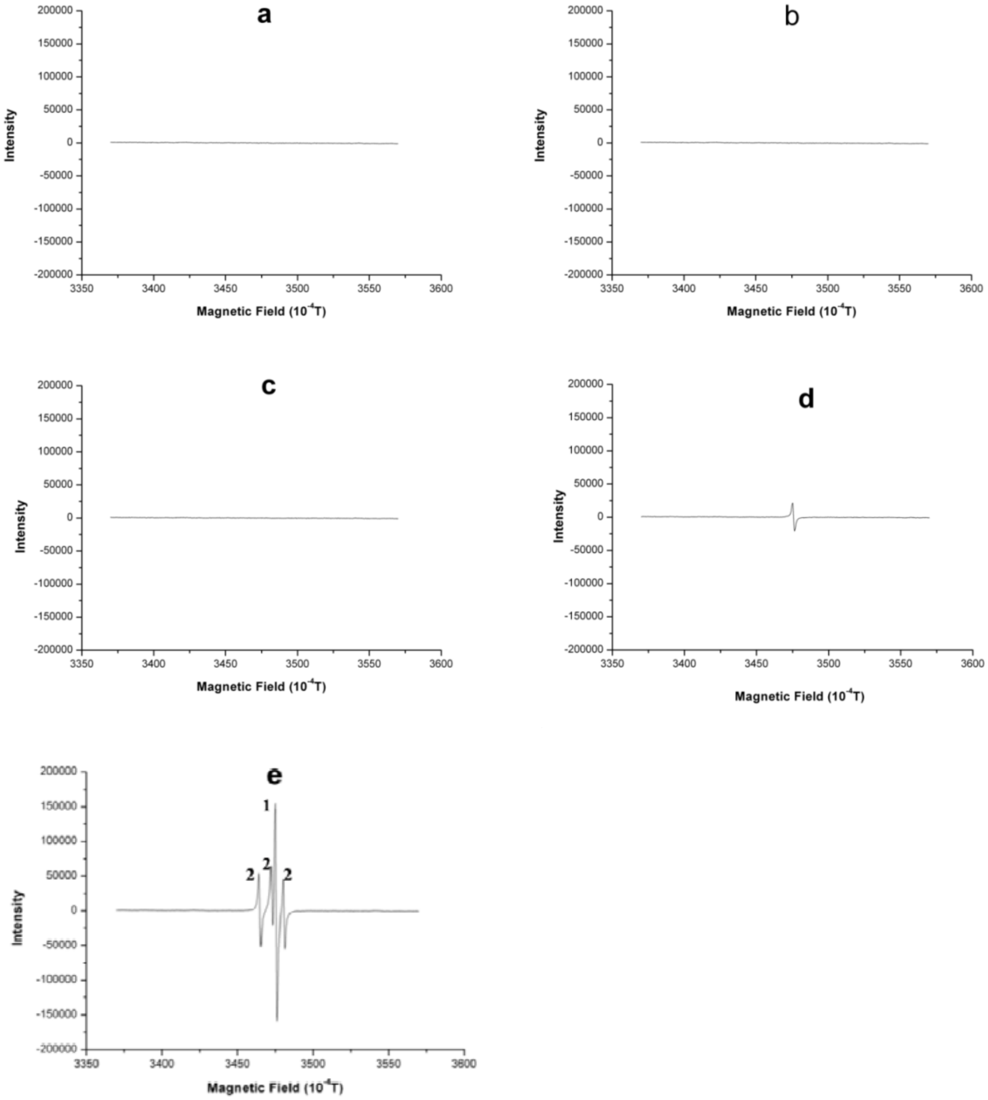


Figure 1. **ESR spectra of five samples.**

a. ESR spectra of reaction system: PBN (0.05 mmol) was dissolved in benzene (1 mL). The mixture showed no signal.

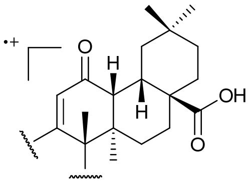
b. ESR spectra of reaction system: CDDO (0.2 mmol) was dissolved in benzene (2 mL) and then refluxed for 30min. The refluxed mixture showed no signal.

c. ESR spectra of reaction system: DDQ (0.2 mmol) was dissolved in benzene (2 mL) and then refluxed for 30min. The refluxed mixture showed no signal.

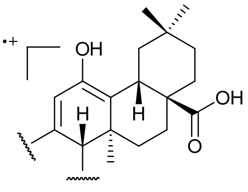
d. ESR spectra of reaction system: CDDO (0.2 mmol) and DDQ (0.2 mmol) was dissolved in benzene (2 mL) and was refluxed for 30min. A free radical signal was detected.

e. ESR spectra of reaction system: CDDO (0.2 mmol) and DDQ (0.2 mmol) was dissolved in benzene (2 mL). The mixture was refluxed for 30min, and cooled to 40 °C (because PBN is unstable at 80 °C.). PBN (0.15 mmol) in 1mL benzene was added to the solution. A heightened and split ESR free radical signal was detected.

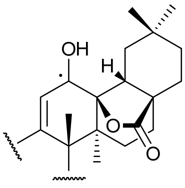
According to our proposed radical ion mechanism by which olean-28,13*β*-olide is formed, there are three possible radical ions and two possible radicals which could generate ESR signals in the reaction system, and they are intermediates **c**, **d**, **e**, DDQ$^{\bullet-}$ and DDQH$^{\bullet}$ as depicted as follows.



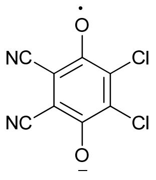
intermediate **c**



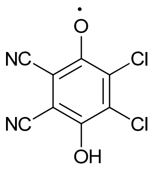
intermediate **d**



intermediate **e**

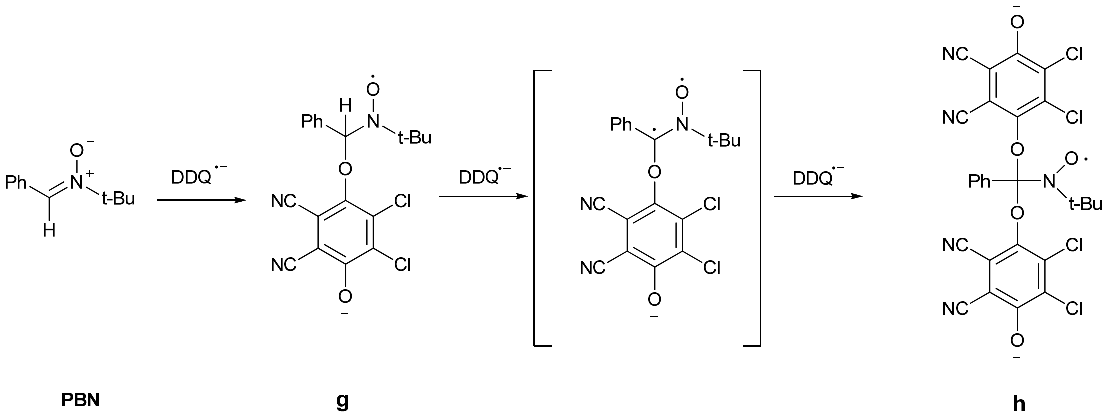


DDQ$^{\bullet-}$



DDQH$^{\bullet}$

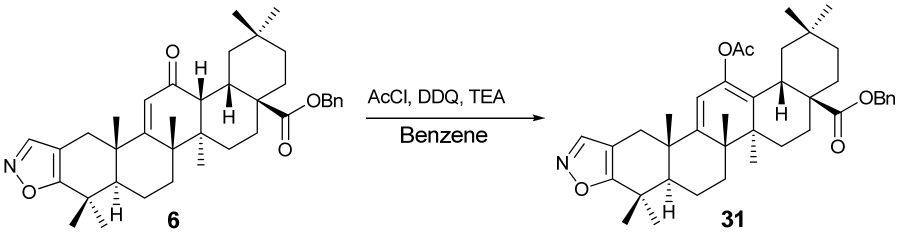
Since DDQ$^{\bullet-}$ is a much more stable radical anion,[5] therefore, the singlet in Figure 1d is assigned to DDQ$^{\bullet-}$; and Figure 1e is composed of two types of signals which are overlapped: e1 and e2, the singlet e1 is attributed to DDQ$^{\bullet-}$, and the triplet e2 is assigned to **h** which generates from the interaction of PBN with DDQ$^{\bullet-}$ illustrated as follows.



5. Enol intermediate trapping experiment

To find more convincing evidence for an enol as a transient intermediate in the formation of lactone, the reaction of excess acetyl chloride with a solution of DDQ and **6** was carried out (**6** is a C28-carboxyl protected derivative of **7**, and **7** can be converted to olean-28,13*β*-olide **8**).

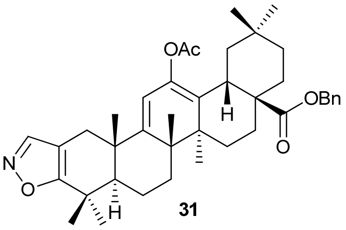
Table 2. Evidence for an enol as a transient intermediate in the DDQ-promoted formation of olean-28,13*β*-olide.[a]



Entry	**6** (equiv.)	DDQ (equiv.)	AcCl (equiv.)	Temp.(°C)	Yield of **31** (%)[b]
1	1.0	-	20	80	-
2	1.0	1.0	20	25	-
3	1.0	1.0	1.0	80	trace
4	1.0	1.0	20	80	2.6

[a] All reactions were run for 48 h. [b] Yield of the isolated product

Benzyl 12-acetoxyisoxazolo[4,5-b]olean-9(11),12(13)-dien-28-oate (31)



31

A mixture of **6** (1.0 g, 1.72 mmol), DDQ (0.39 g, 1.72 mmol), acetyl chloride (0.69 g, 34.4 mmol) and triethylamine (0.20 g, 2.0 mmol) in anhydrous benzene (60 mL) was refluxed for 48 h. After filtration, the filtrate was evaporated in vacuo to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc) to give **31** as an amorphous solid (28 mg, 2.6%).

m.p. 74-76 °C;

IR (KBr, cm^{-1}): 3434, 2947, 2861, 2353, 2312, 1722, 1660, 1581, 1456, 1384;

ESI-MS: 526 $[M+H]^+$;

^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ 8.02 (s, 1H), 7.34-7.30 (m, 5H), 5.58 (s, 1H), 5.20 (d, *J* =

12.5 Hz, 1H), 5.02 (d, J = 12.5 Hz, 1H), 3.35 (m, 1H), 2.76 (d, J = 15 Hz, 1H), 2.43 (d, J = 15 Hz, 1H) , 1.37, 1.26, 1.12, 1.01, 0.99, 0.95, 0.90 (s, each 3H) ppm;

^{13}C NMR (75M Hz, $CDCl_3$, 25 °C, TMS): δ 176.9, 172.7, 169.3, 154.1, 150.2, 140.7, 136.4, 129.3, 128.6, 128.4, 128.2, 128.1, 127.9, 116.8, 109.2, 66.1, 50.6, 45.4, 43.4, 41.6, 40.5, 40.2, 35.0, 34.4, 33.8, 32.8, 32.7, 32.1, 30.9, 30.5, 28.9, 27.1, 25.6, 23.3, 23.2, 21.2, 20.7, 20.0, 19.4, 18.5;

HRMS (EI^+) calc. for $[C_{40}H_{51}NO_5Na]^+$ 648.3665, found 648.3669.

6. Cytotoxicity assay

Human hepatoma (BEL-7402) cell, human cervical cancer (HeLa) cells, human breast cancinoma (MCF-7) cell (all from Shanghai Institutes for Biological Science, Chinese Academy of Science) were cultivated at 37 °C, 5% CO_2 in DMEM medium with 10% heat inactivated fetal calf serum (all from Gibco, USA). *In vitro* inhibitory effects of the target compounds on the cells were measured by MTT assay. The cells treated with Trypsin-EDTA solution were placed in 96-well plates for 24 h and incubated with individual compounds at different concentrations in the vehicle (0.1% DMSO) or in vehicle alone for 48 h. Then the cells were exposed to MTT (5 mg/ml, sigma) for 4 h and the resulting formazan crystals were dissolved in 200 μM DMSO and measured at 570 nm on a microplate reader (Thermo, USA). The absorbance data were converted into a cell proliferation percentage, in comparison with DMSO treated cells, to determine growth inhibition. Each assay was performed in triplicate.

7. The references of the electronic supplementary information

1 Y. Ding, Z. Huang, J. Yin, S. Zhang, Y. Lai, S. Peng and Y. Zhang, *Synthesis*, 2011, submitted.

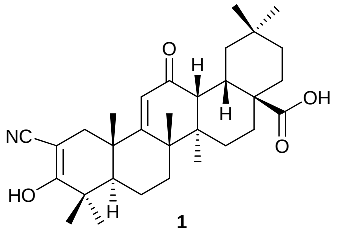
2. T. Honda, B.V. Rounds, L. Bore, H. J. Finlay, F. G. Favaloro, N. Suh, Y. Wang, M. B. Sporn and G. W. Gribble, *J. Med. Chem*., 2000, **43**, 4233.

3. J. Li, S. Chen, Y. Zhao and J. Li, *Carbohydr. Res.*, 2009, **344**, 599.

4. F. King, C. Cotterill, D. Godson, L. Jurd and T. King, *J. Chem. Soc.*, 1953, 3693.

5. G. Grampp, S. Landgraf and K. Rasmussen, *J. Chem. Soc.*, *Perkin Trans. 2.*, 1999, **9**, 1897.

8. ^{1}H NMR and ^{13}C NMR spectra of new compounds



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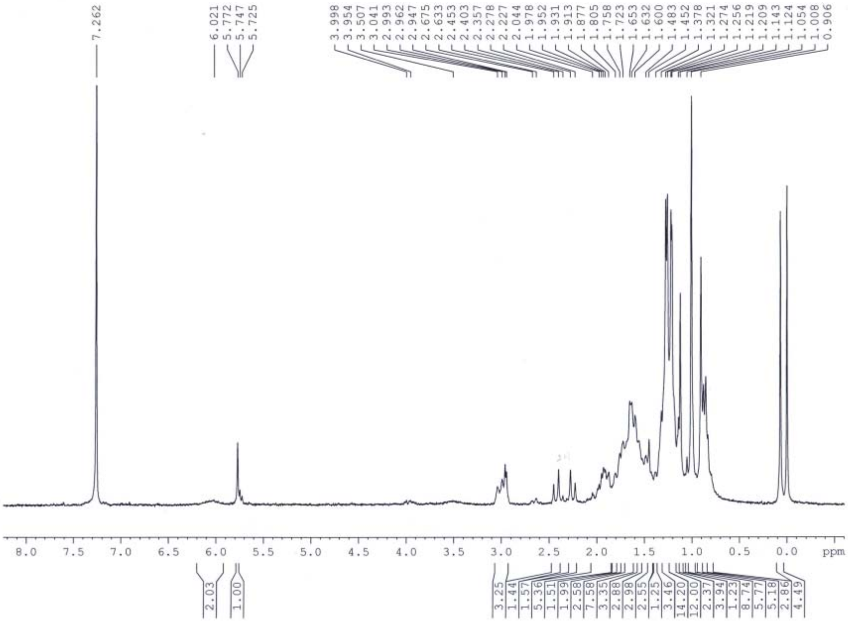

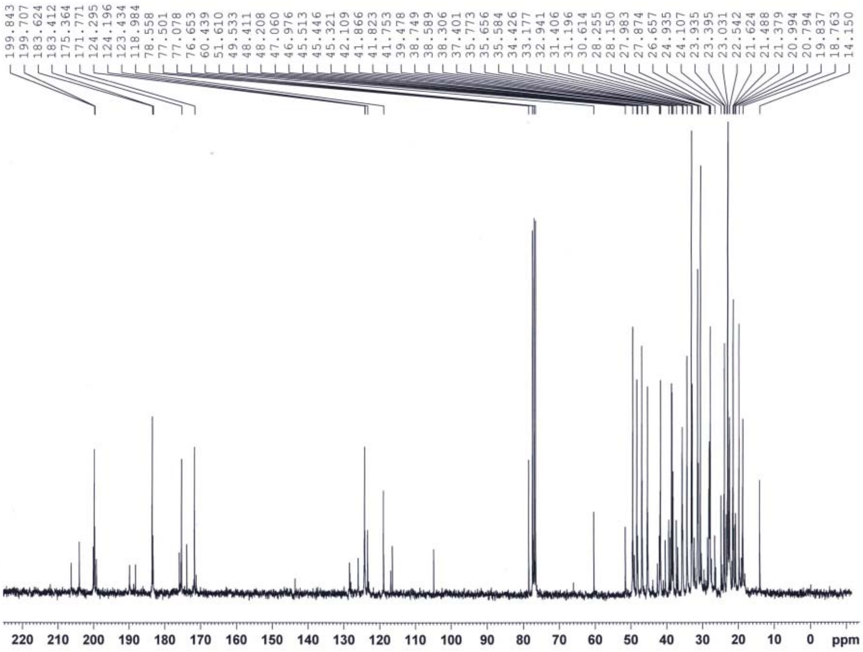

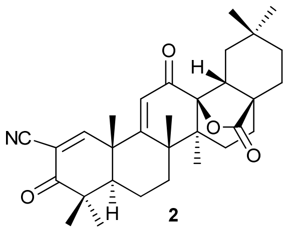
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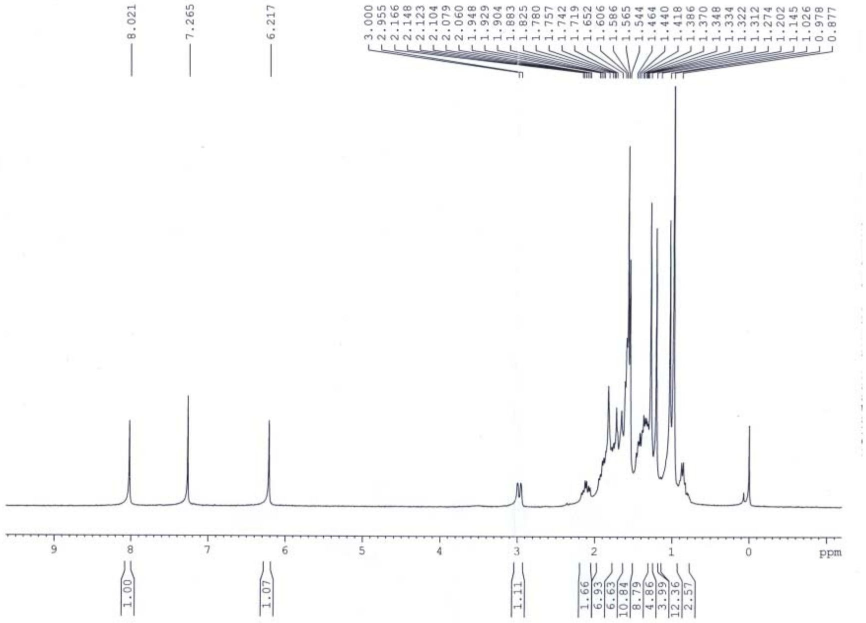
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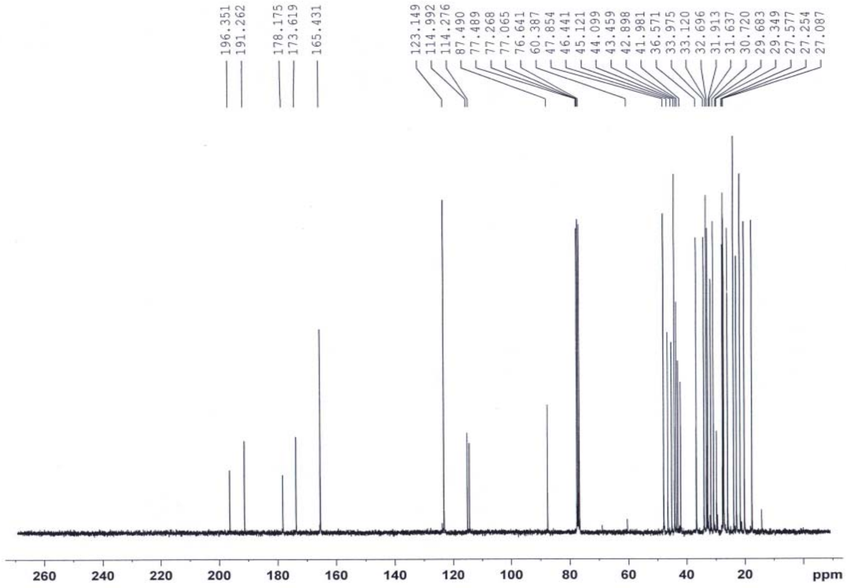
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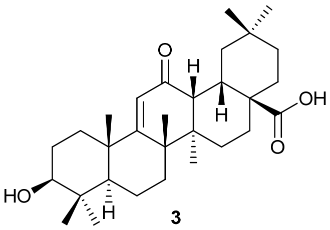
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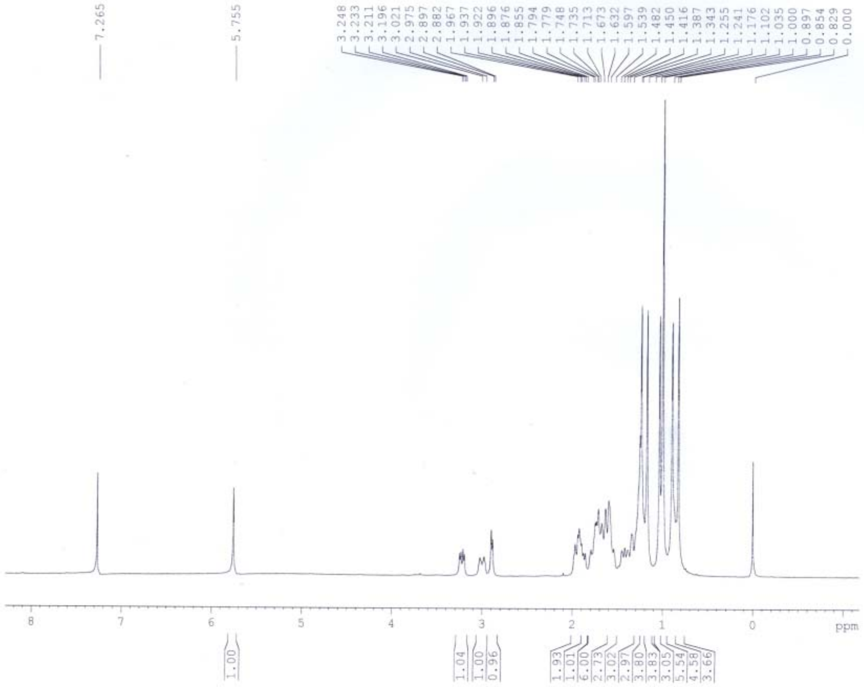
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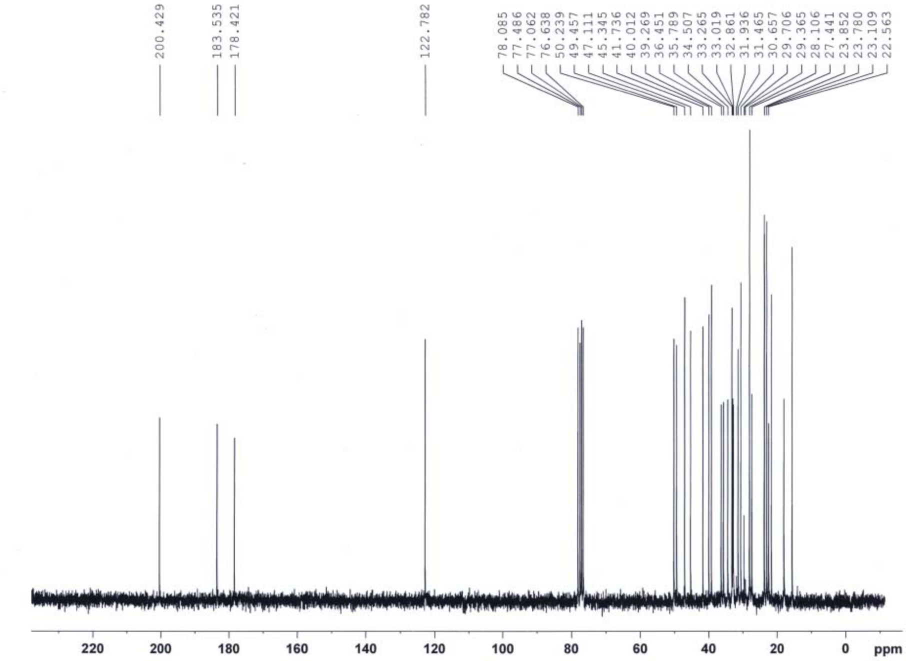
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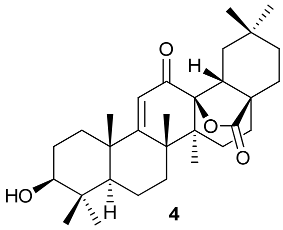
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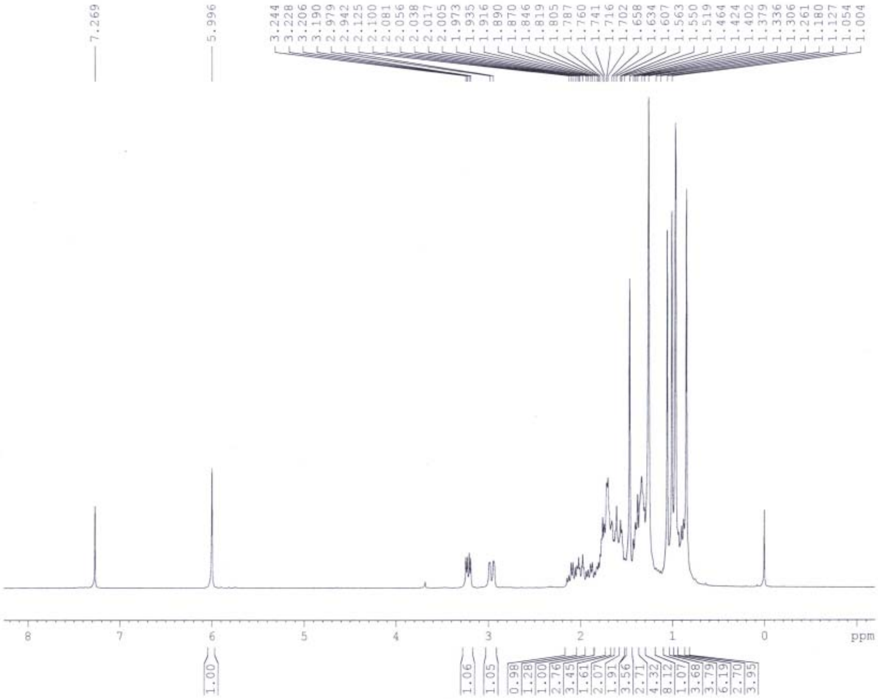
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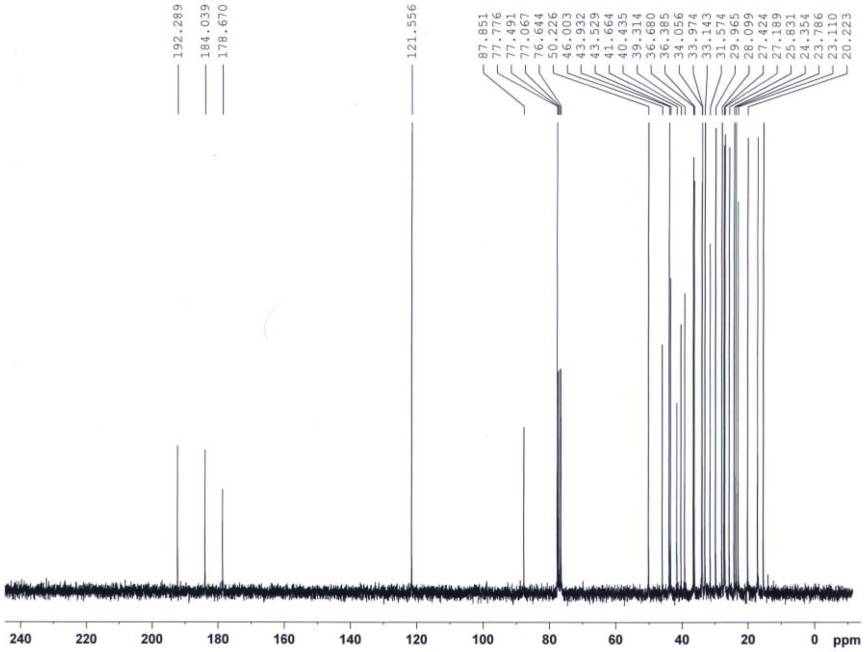
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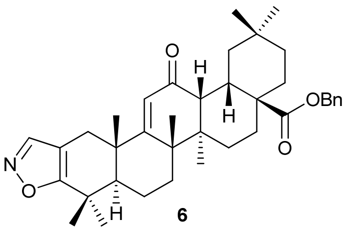
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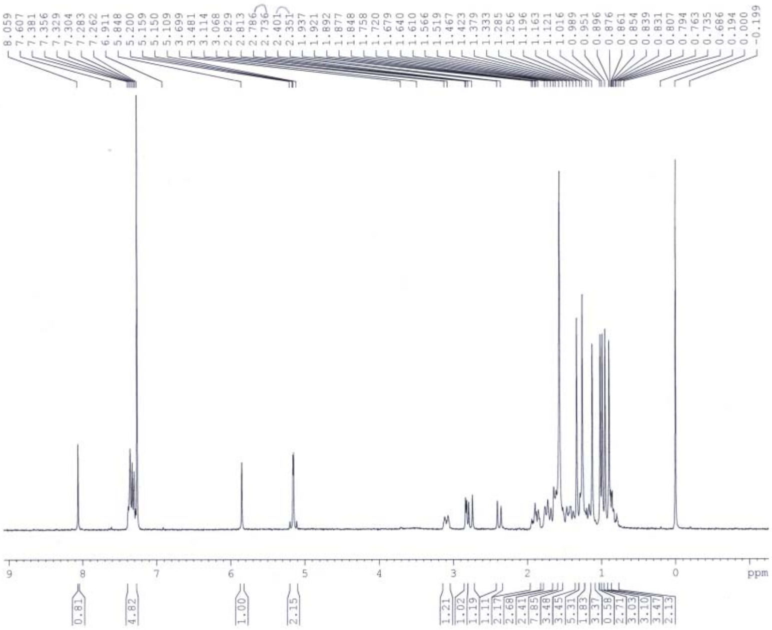
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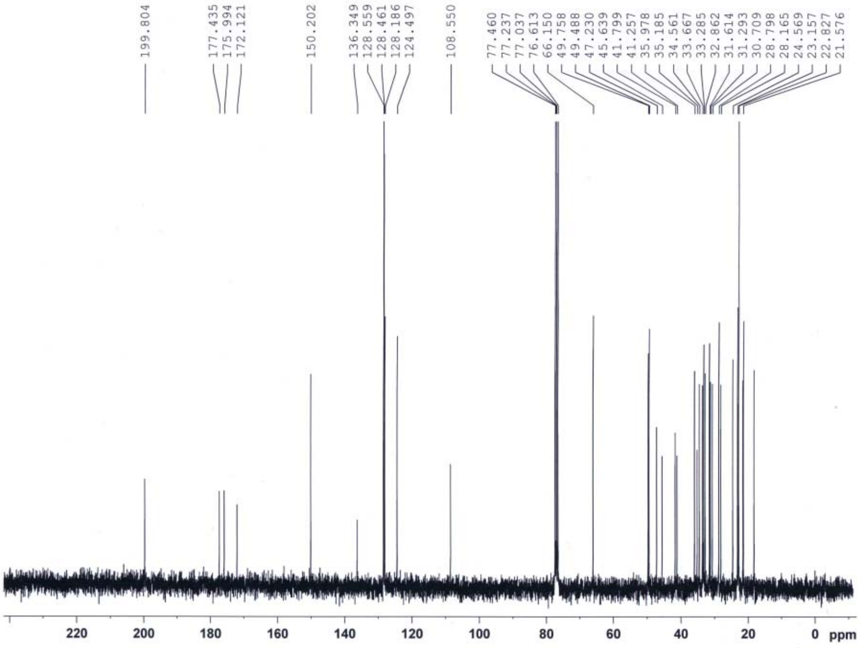
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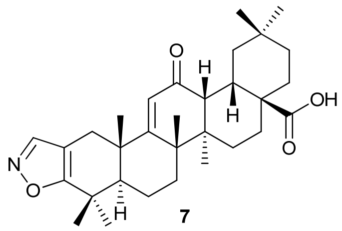
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H
H
OH
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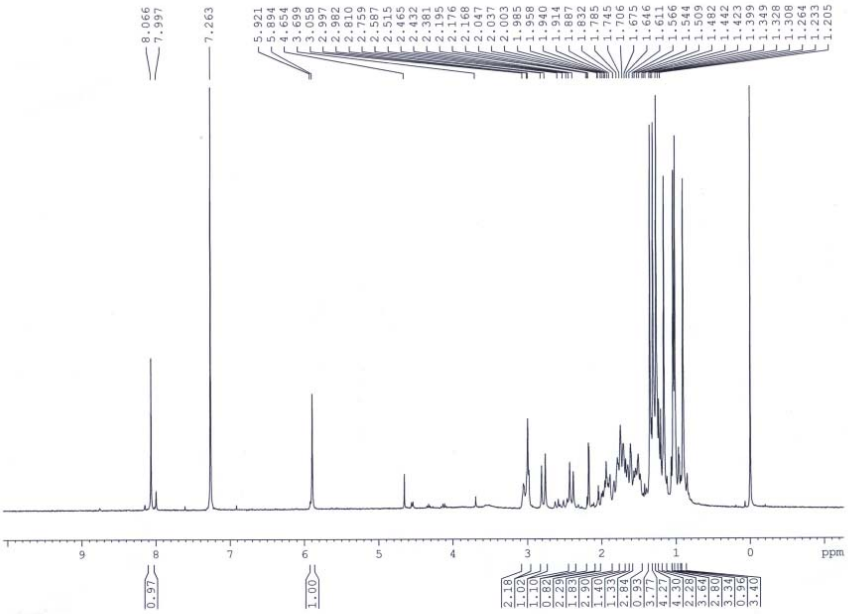
N
O
H

7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4.654
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3.058
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2.982
2.810
2.759
2.587
2.515
2.465
2.432
2.381
2.195
2.176
2.168
2.047
2.037
2.003
1.985
1.958
1.940
1.914
1.887
1.832
1.785
1.745
1.706
1.675
1.646
1.611
1.566
1.544
1.509
1.482
1.442
1.423
1.399
1.349
1.328
1.308
1.264
1.233
1.205
9
8
7
6
5
4
3
2
1
0
ppm
0.97
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2.18
1.02
1.10
0.82
2.29
1.83
2.90
1.40
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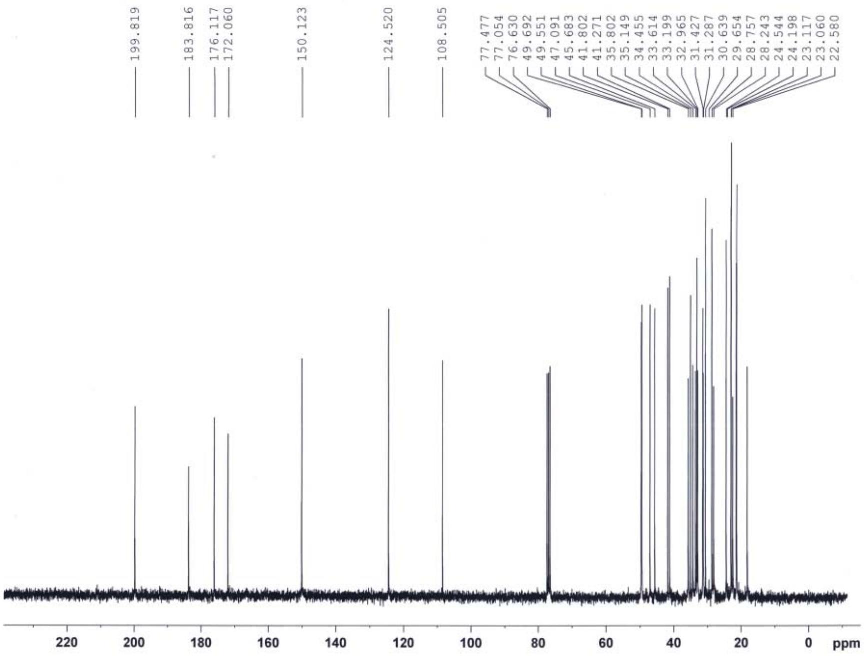
3.40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124.520
108.505
77.477
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76.630
49.692
49.551
47.091
45.683
41.802
41.271
35.802
35.149
34.455
33.614
33.199
32.965
31.427
31.287
30.639
29.654
28.757
28.243
24.544
24.198
23.117
23.060
22.580
220
200
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140
120
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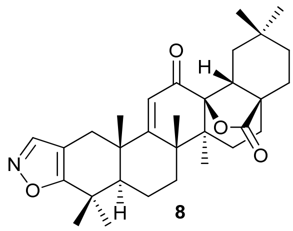
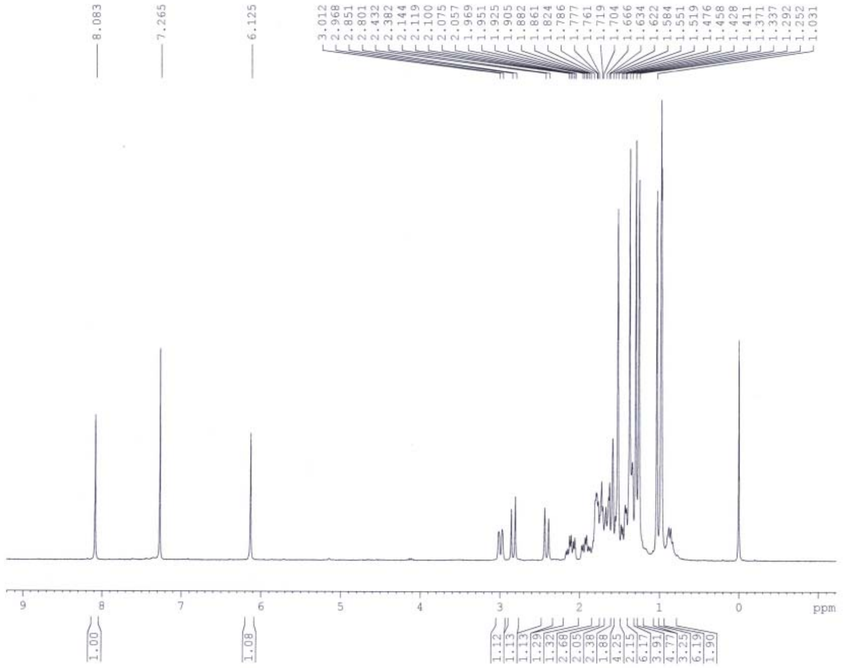
60
40
20
0
ppm


O
H
O
O
N
O
H

8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2.968
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2.801
2.432
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2.144
2.119
2.100
2.075
2.057
1.969
1.951
1.925
1.905
1.882
1.861
1.824
1.786
1.777
1.761
1.719
1.704
1.666
1.634
1.622
1.584
1.551
1.519
1.476
1.458
1.428
1.411
1.371
1.337
1.292
1.252
1.031
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.08
1.12
1.13
1.13
1.29
1.32
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2.15
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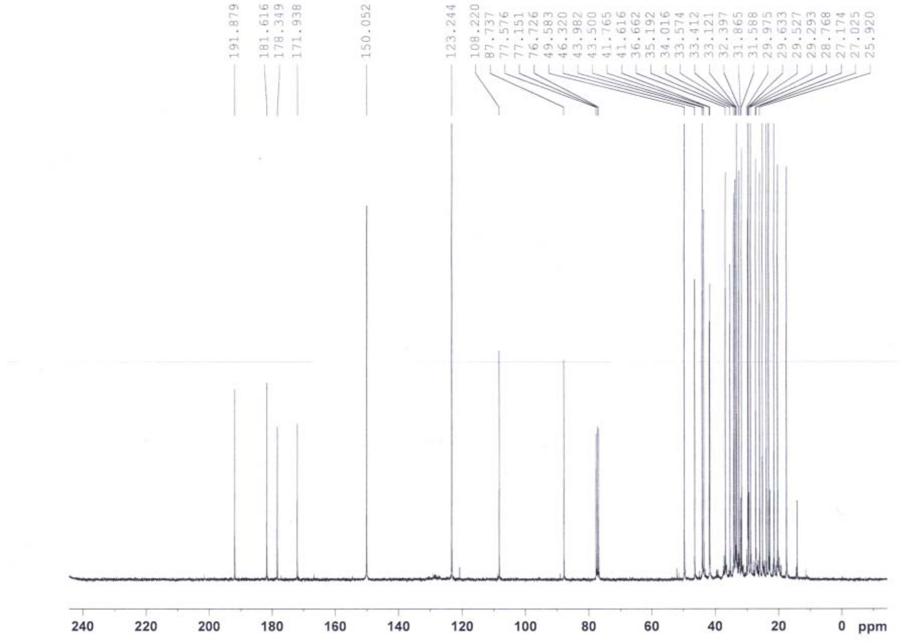
3.91
4.77
3.25
6.19
1.90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108.220
87.737
77.576
77.151
76.726
49.583
46.320
43.982
43.500
41.765
41.616
36.662
35.192
34.016
33.574
33.412
33.121
32.397
31.865
31.588
29.975
29.633
29.527
29.293
28.768
27.174
27.025
25.920
240
220
200
180
160
140
120
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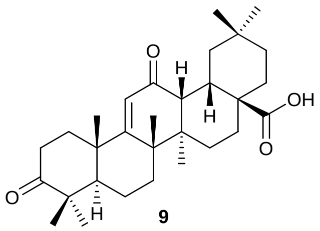
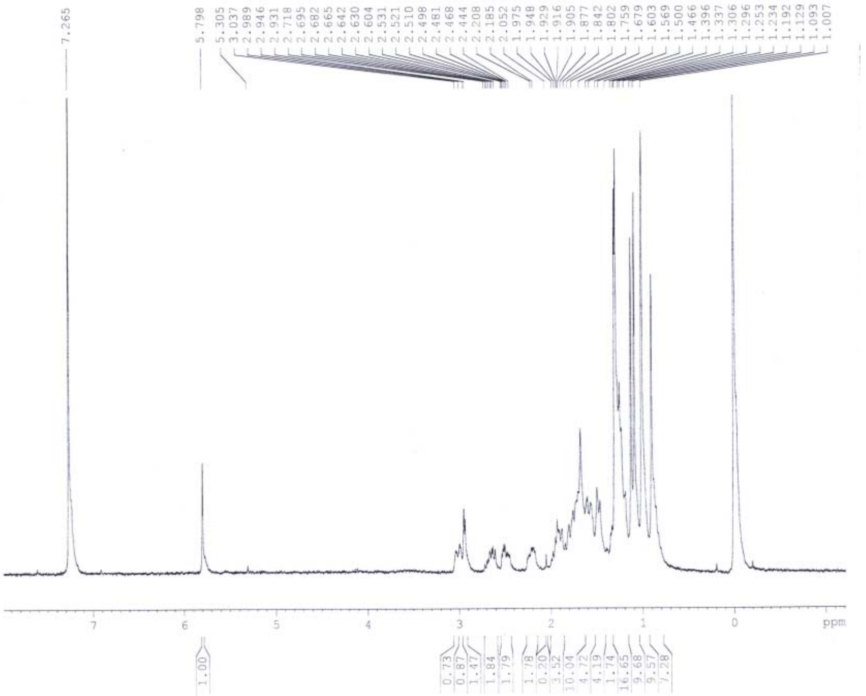
60
40
20
0
ppm


O
H
H
OH
O
O
H

9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3.037
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2.931
2.718
2.695
2.682
2.665
2.642
2.630
2.604
2.531
2.521
2.510
2.498
2.481
2.468
2.444
2.208
2.185
2.052
1.975
1.948
1.929
1.916
1.905
1.877
1.842
1.802
1.759
1.679
1.603
1.569
1.500
1.466
1.396
1.337
1.306
1.296
1.253
1.234
1.192
1.129
1.093
1.007
7
6
5
4
3
2
1
0
ppm
1.00
0.73
0.87
1.47
1.84
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1.78
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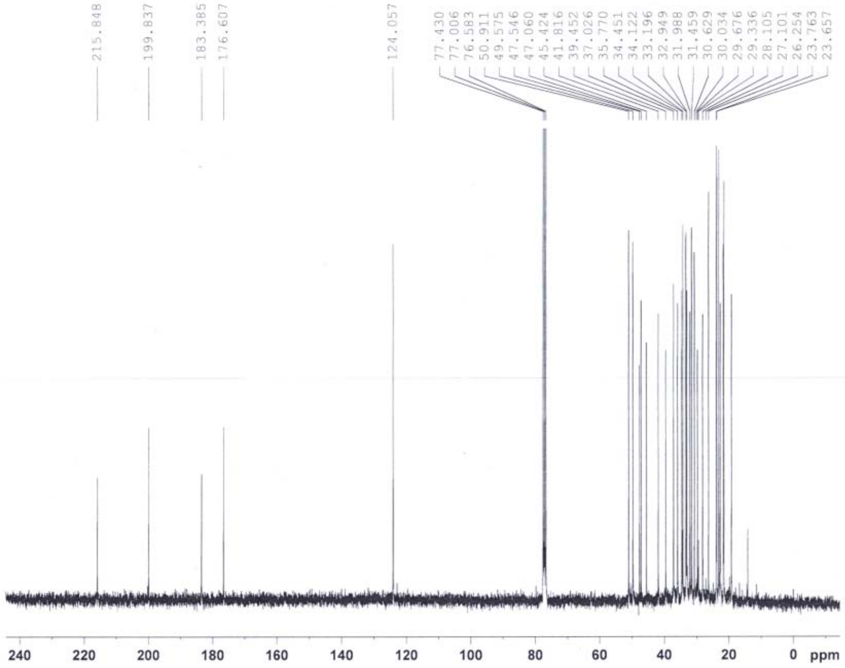
3.52
10.04
4.72
4.19
1.74
16.65
9.68
9.57
7.28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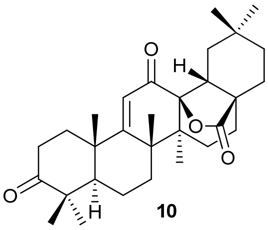
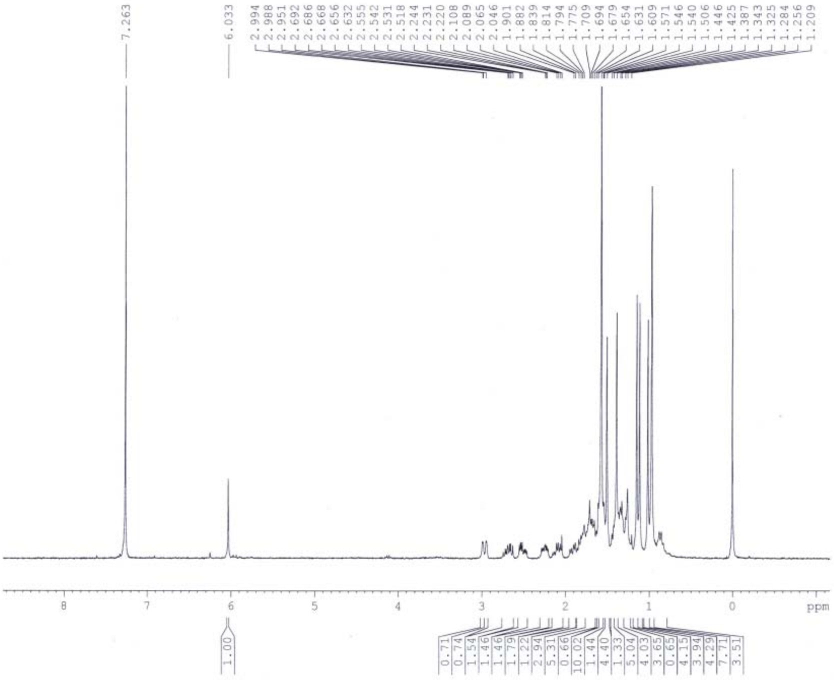
199.837
183.385
176.607
124.057
77.430
77.006
76.583
50.911
49.575
47.546
47.060
45.424
41.816
39.452
37.026
35.770
34.451
34.122
33.196
32.949
31.988
31.459
30.629
30.034
29.676
29.336
28.105
27.101
26.254
23.763
23.657
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm



10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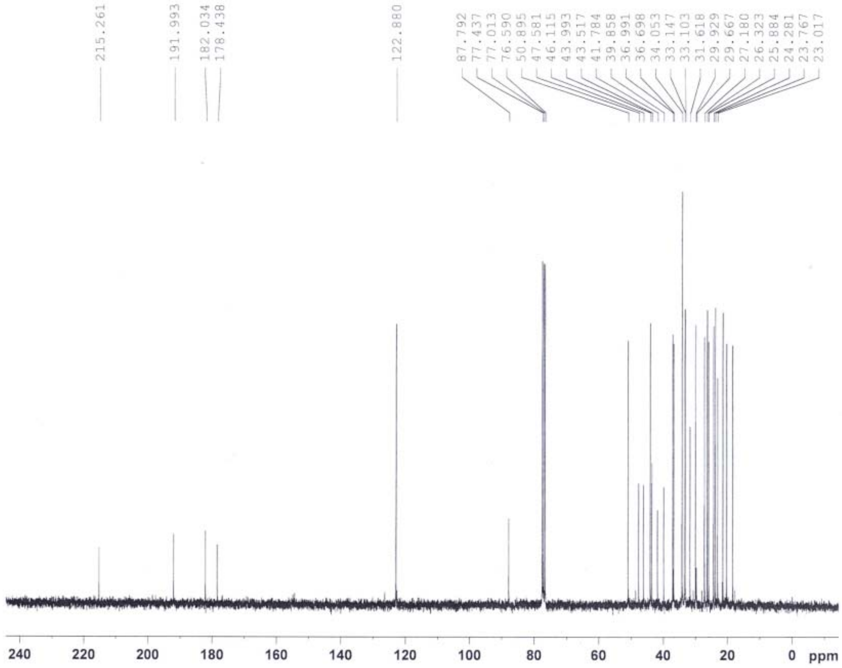
2.692
2.686
2.668
2.656
2.632
2.555
2.542
2.531
2.518
2.244
2.231
2.220
2.108
2.089
2.065
2.046
1.901
1.882
1.839
1.814
1.794
1.775
1.709
1.694
1.679
1.654
1.631
1.609
1.571
1.546
1.540
1.506
1.446
1.425
1.387
1.343
1.325
1.284
1.256
1.209
8
7
6
5
4
3
2
1
0
ppm
1.00
0.71
0.74
1.54
1.46
1.46
1.79
1.22
2.94
5.31
0.66
10.02
1.44
4.40
1.33
5.04
4.03
3.65
0.65
4.15
3.94
4.29
7.71
3.51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77.013
76.590
50.895
47.581
46.115
43.993
43.517
41.784
39.858
36.991
36.698
34.053
33.147
33.103
31.618
29.929
29.667
27.180
26.323
25.884
24.281
23.767
23.017
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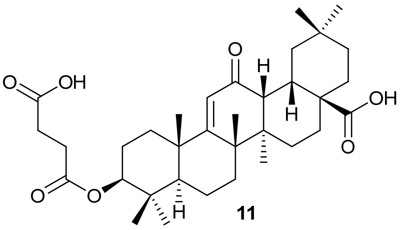
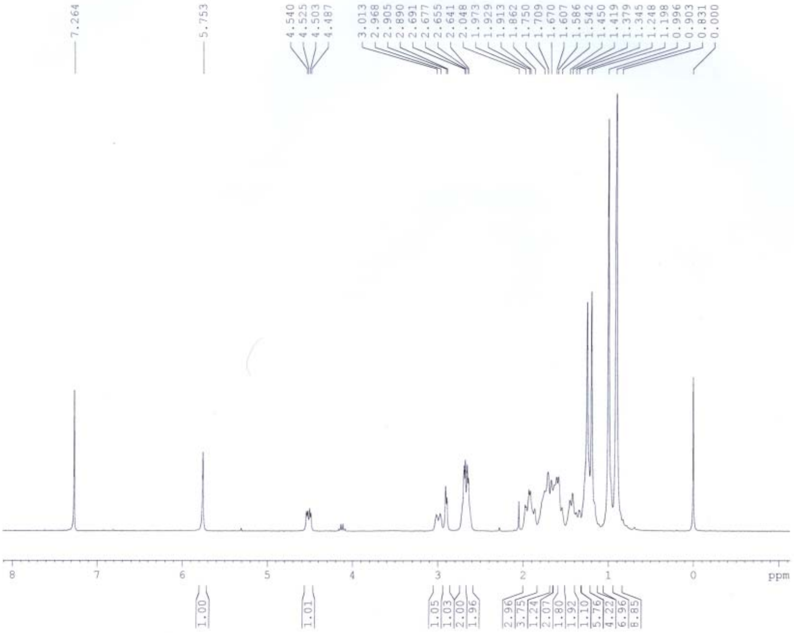
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
OH
O
O
O
H
H
H
OH
O

11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4.503
4.487
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2.905
2.890
2.691
2.677
2.655
2.641
2.048
1.973
1.929
1.913
1.862
1.750
1.709
1.670
1.607
1.586
1.542
1.450
1.419
1.379
1.345
1.248
1.198
0.996
0.903
0.831
0.000
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.05
1.03
2.00
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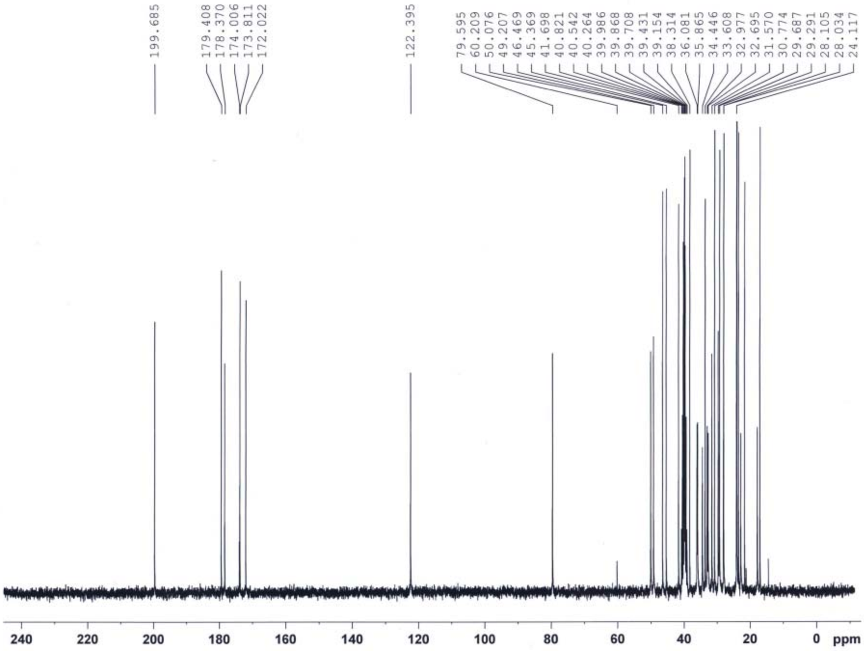
2.96
3.75
1.24
2.07
1.80
1.92
1.10
5.76
4.22
6.96
8.85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50.076
49.207
46.469
45.369
41.698
40.821
40.542
40.264
39.986
39.868
39.708
39.431
39.154
38.314
36.081
35.865
34.446
33.608
32.977
32.695
31.570
30.774
29.687
29.291
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28.034
24.117
240
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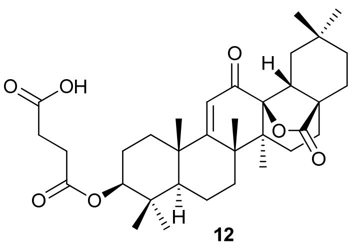
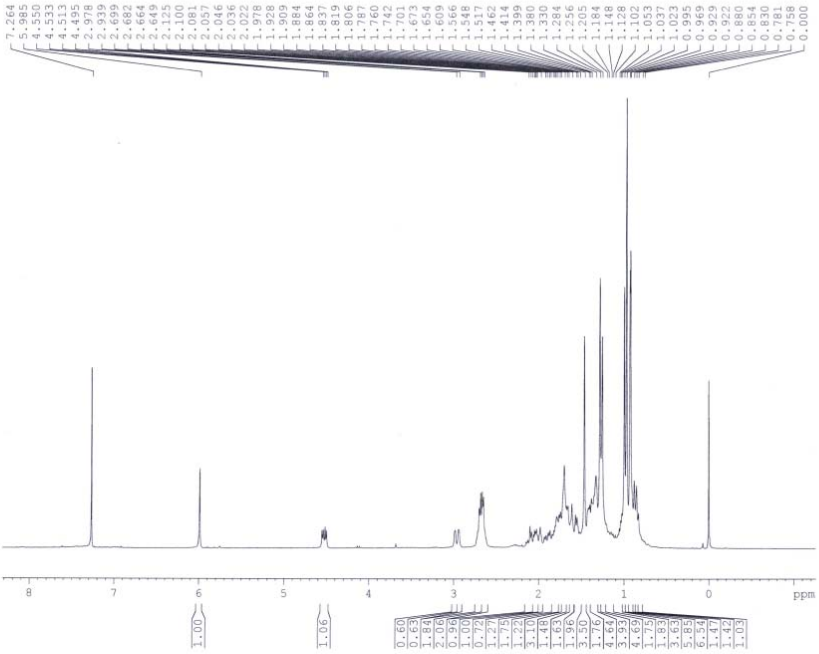
200
180
160
140
120
100
80
60
40
20
0
ppm


O
OH
O
O
O
H
O
O
H

12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4.513
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2.939
2.699
2.682
2.664
2.649
2.125
2.100
2.081
2.057
2.046
2.036
2.022
1.978
1.928
1.909
1.884
1.864
1.837
1.819
1.806
1.787
1.760
1.742
1.701
1.673
1.654
1.609
1.566
1.548
1.517
1.462
1.414
1.399
1.380
1.330
1.284
1.256
1.205
1.184
1.148
1.128
1.102
1.053
1.037
1.023
0.995
0.969
0.929
0.922
0.880
0.854
0.830
0.781
0.758
0.000
8
7
6
5
4
3
2
1
0
ppm
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1.06
0.60
0.63
1.84
2.06
0.96
1.00
0.72
1.27
1.75
1.22
3.10
1.48
1.63
1.96
3.50
1.76
4.64
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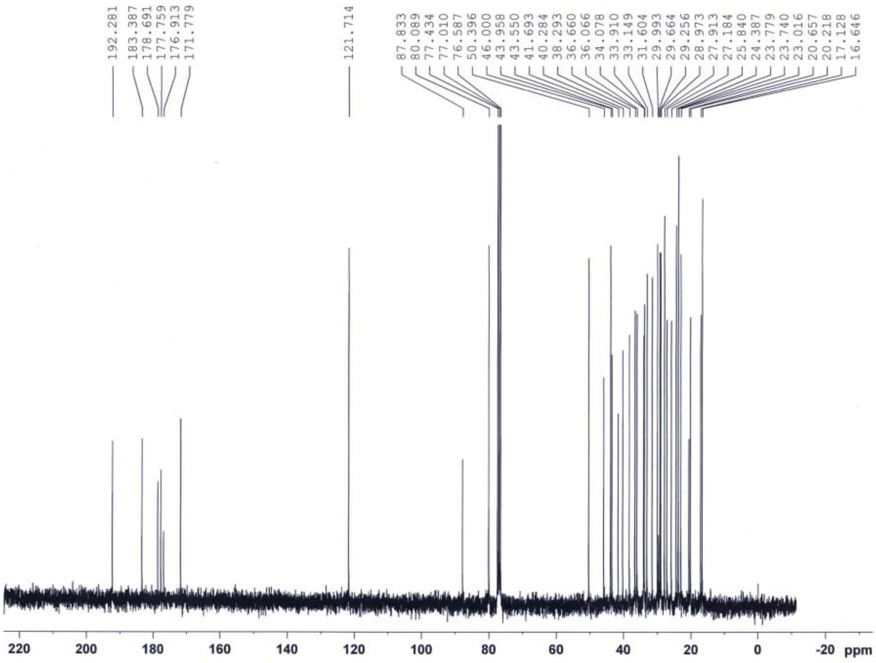
4.69
1.75
1.83
3.63
5.85
6.54
1.47
1.42
1.03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176.913
171.779
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87.833
80.089
77.434
77.010
76.587
50.396
46.000
43.958
43.550
41.693
40.284
38.293
36.660
36.066
34.078
33.910
33.149
31.604
29.993
29.664
29.256
28.973
27.913
27.184
25.840
24.387
23.779
23.740
23.016
20.657
20.218
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16.646
220
200
180
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140
120
100
80
60
40
20
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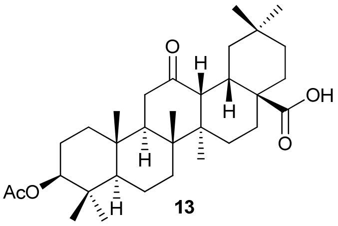
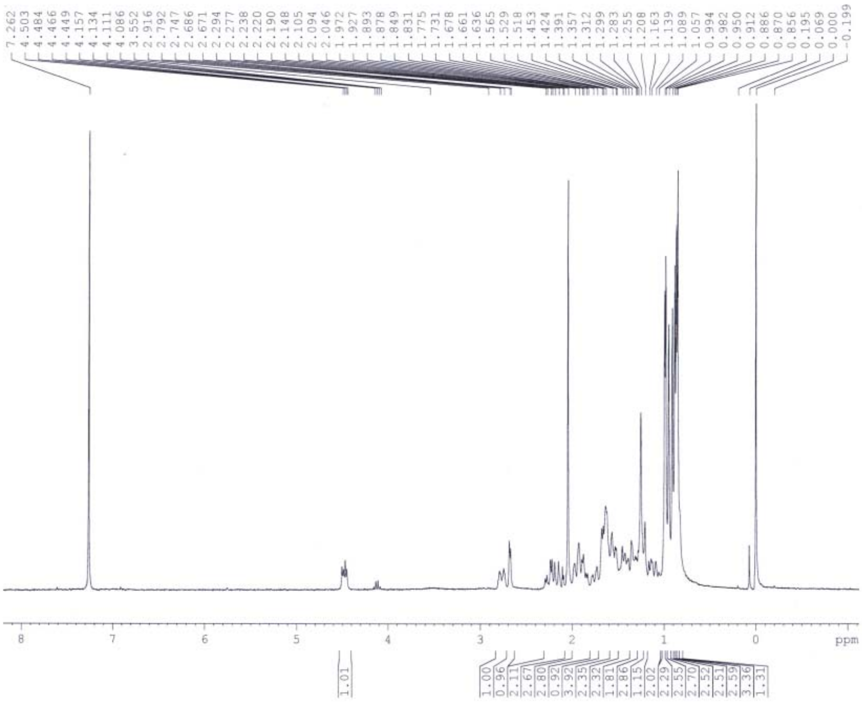
-20
ppm


O
H
H
OH
O
H
AcO
H

13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4.134
4.111
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3.552
2.916
2.792
2.747
2.686
2.671
2.294
2.277
2.238
2.220
2.190
2.148
2.105
2.094
2.046
1.972
1.927
1.893
1.878
1.849
1.831
1.775
1.731
1.678
1.661
1.636
1.565
1.529
1.518
1.453
1.424
1.391
1.357
1.312
1.299
1.283
1.255
1.208
1.163
1.139
1.089
1.057
0.994
0.982
0.950
0.912
0.886
0.870
0.856
0.195
0.069
0.000
-0.199
8
7
6
5
4
3
2
1
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ppm
1.01
1.00
0.96
2.11
2.67
2.80
0.92
3.92
2.35
2.32
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2.02
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2.55
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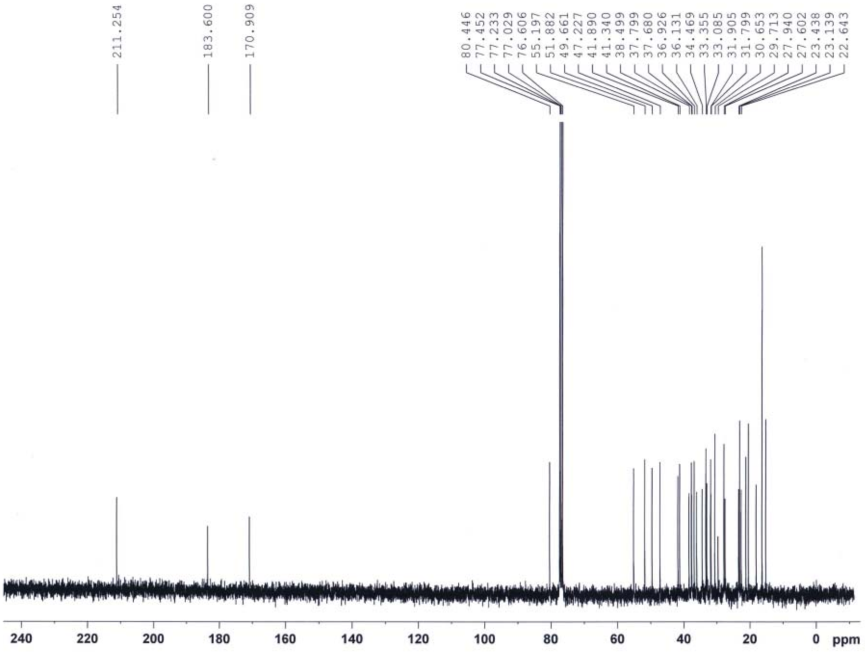
2.51
2.59
3.36
1.31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80.446
77.452
77.233
77.029
76.606
55.197
51.882
49.661
47.227
41.890
41.340
38.499
37.799
37.680
36.926
36.131
34.469
33.355
33.085
31.905
31.799
30.653
29.713
27.940
27.602
23.438
23.139
22.643
240
220
200
180
160
140
120
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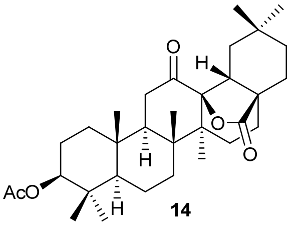
60
40
20
0
ppm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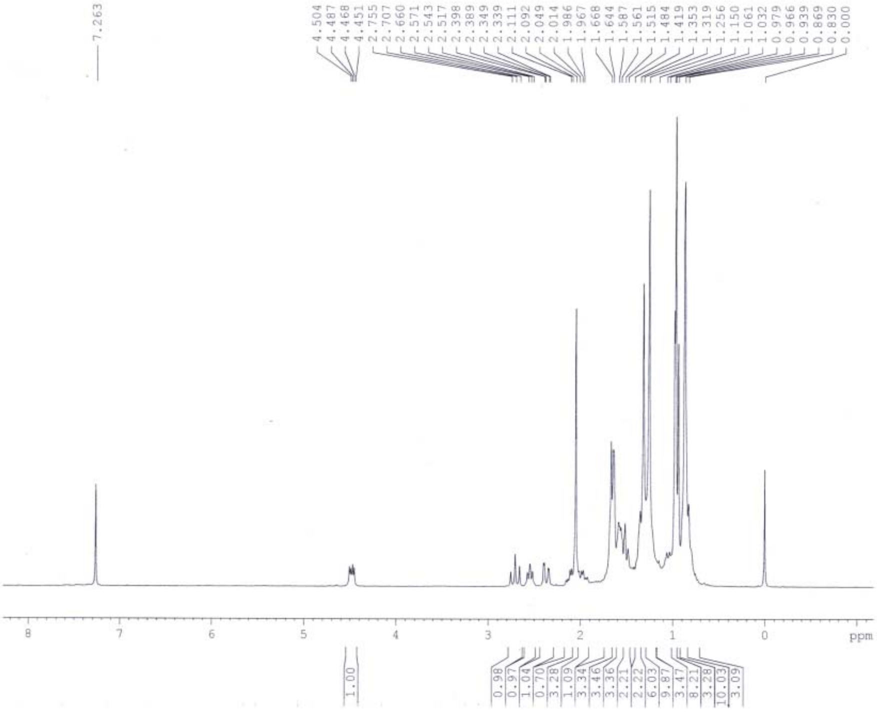
H
O
O
H
AcO
H

14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4.468
4.451
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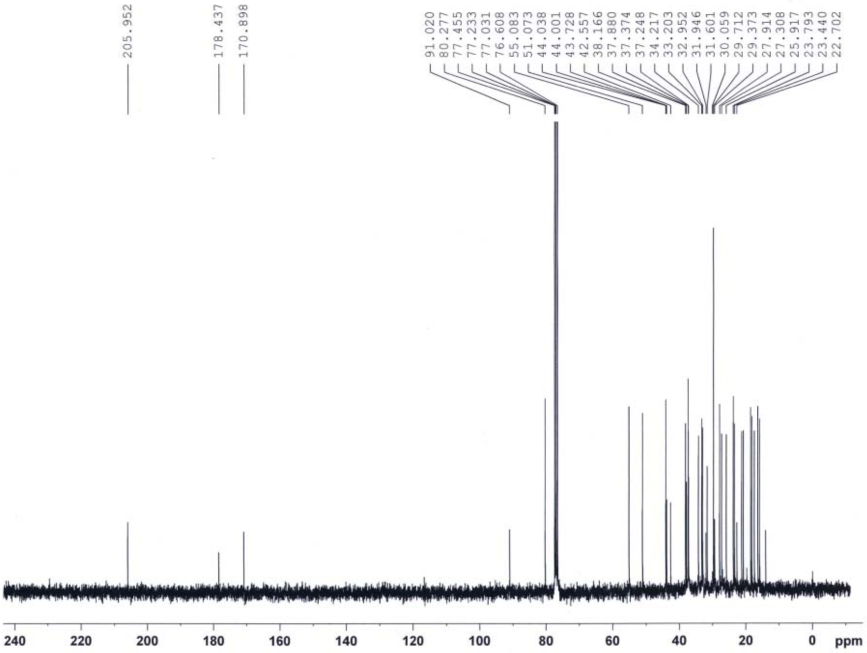
2.707
2.660
2.571
2.543
2.517
2.398
2.389
2.349
2.339
2.111
2.092
2.049
2.014
1.986
1.967
1.668
1.644
1.587
1.561
1.515
1.484
1.419
1.353
1.319
1.256
1.150
1.061
1.032
0.979
0.966
0.939
0.869
0.830
0.000
8
7
6
5
4
3
2
1
0
ppm
1.00
0.98
0.97
1.04
0.70
3.28
1.09
3.34
3.46
3.36
2.21
2.22
6.03
9.87
3.47
8.21
3.28
10.03
3.09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170.898
91.020
80.277
77.455
77.233
77.031
76.608
55.083
51.073
44.038
44.001
43.728
42.557
38.166
37.880
37.374
37.248
34.217
33.203
32.952
31.946
31.601
30.059
29.712
29.373
27.914
27.308
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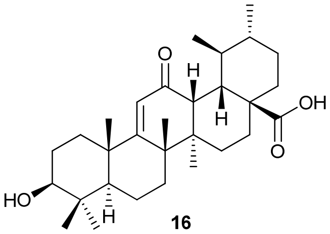
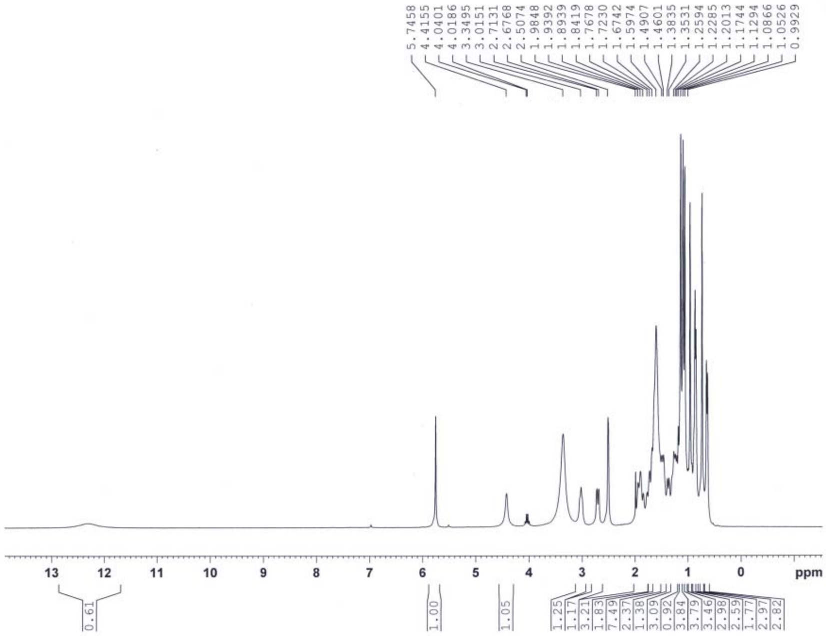
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
H
H
OH
O
HO
H

16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4.0186
3.3495
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2.7131
2.6768
2.5074
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1.9392
1.8939
1.8419
1.7678
1.7230
1.6742
1.5974
1.4907
1.4601
1.3835
1.3531
1.2594
1.2285
1.2013
1.1744
1.1294
1.0866
1.0526
0.9929
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.61
1.00
1.05
1.25
1.17
3.21
1.83
7.49
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1.38
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0.92
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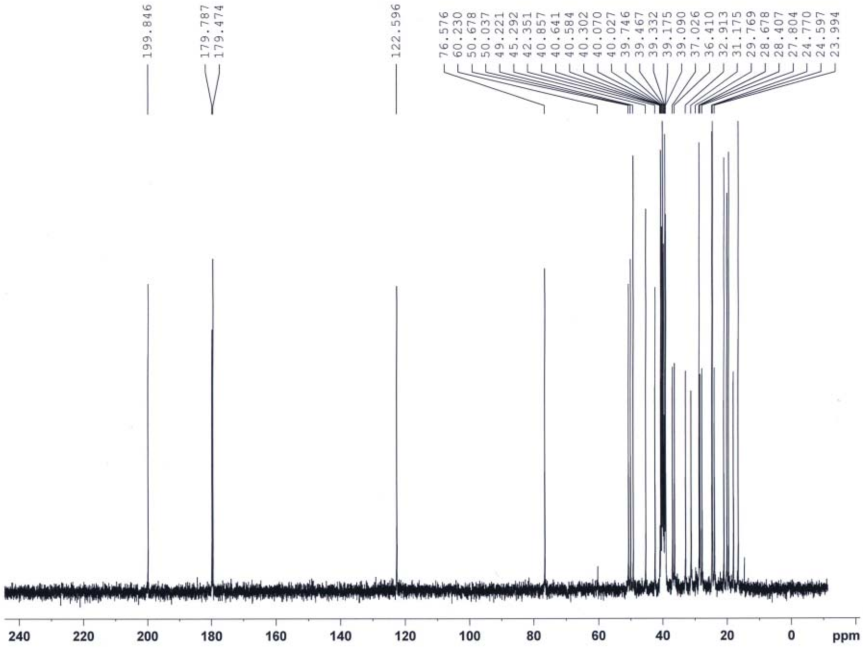
3.79
3.46
2.98
2.59
1.77
2.97
2.82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179.787
179.474
122.596
76.576
60.230
50.678
50.037
49.221
45.292
42.351
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40.070
40.027
39.746
39.467
39.332
39.175
39.090
37.026
36.410
32.913
31.175
29.769
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28.407
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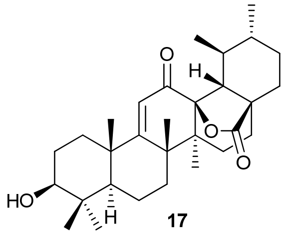
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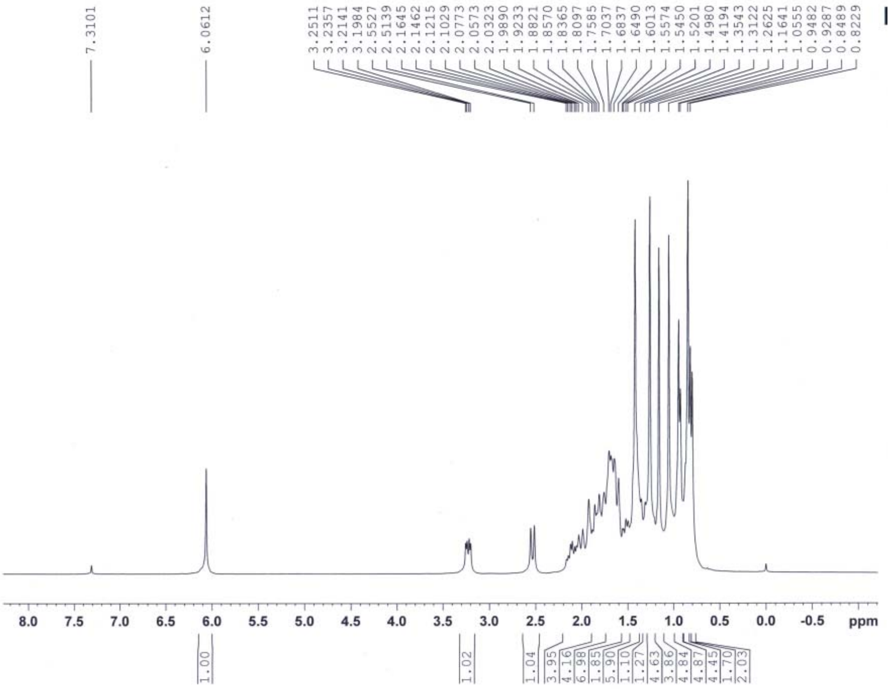
HO
H

17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2.0773
2.0573
2.0323
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1.8821
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1.8365
1.8097
1.7585
1.7037
1.6837
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1.6013
1.5574
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1.5201
1.4980
1.4194
1.3543
1.3122
1.2625
1.1641
1.0555
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0.9287
0.8489
0.8229
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.0
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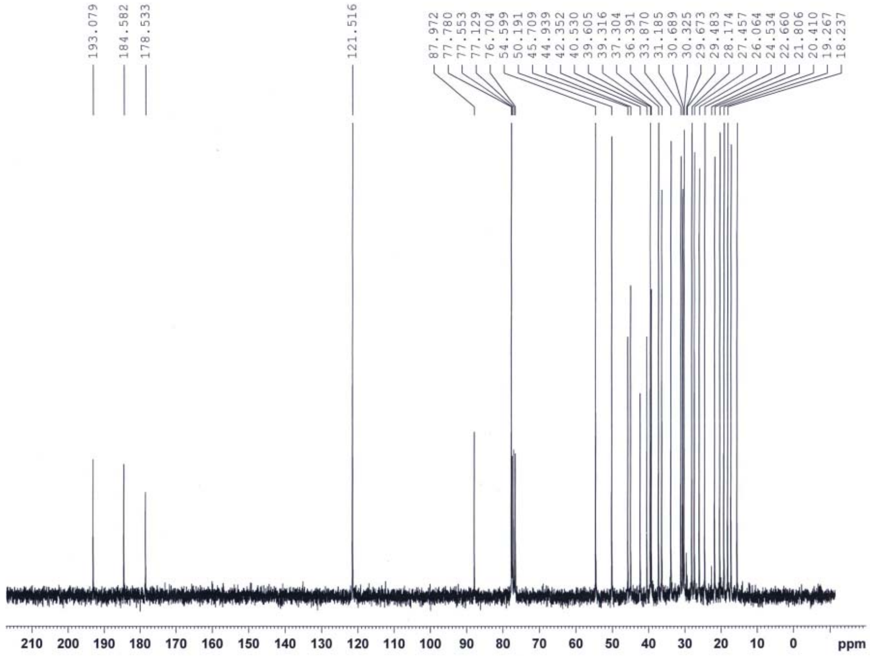
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42.352
40.530
39.605
39.316
37.304
36.391
33.870
31.185
30.689
30.325
29.673
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28.174
27.457
26.064
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20.410
19.267
18.237
210
200
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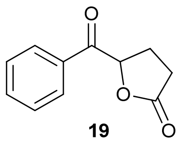
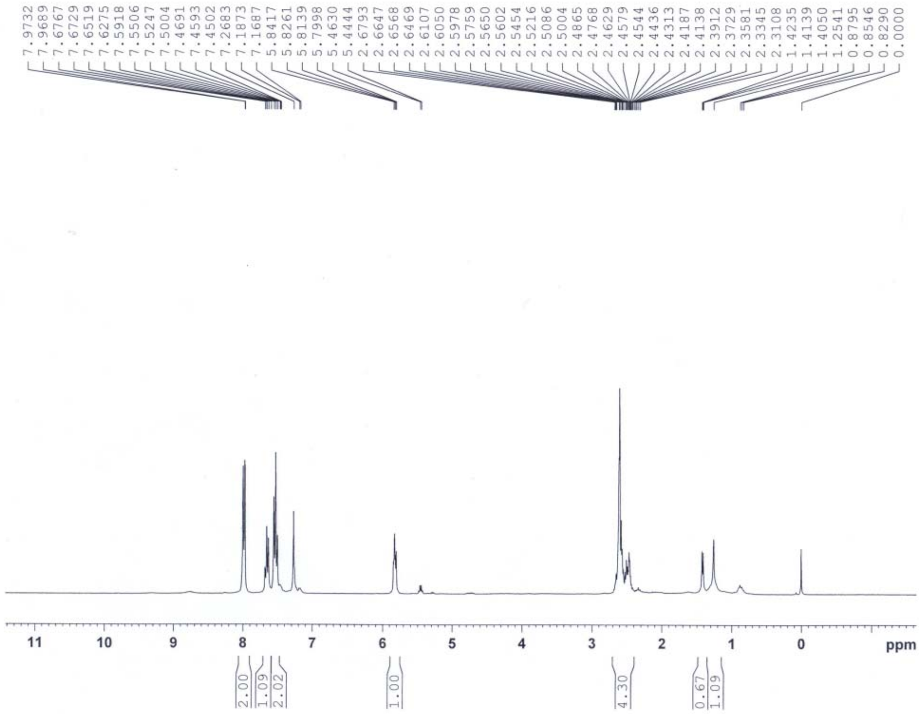


19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7.4593
7.4502
7.2683
7.1873
7.1687
5.8417
5.8261
5.8139
5.7998
5.4630
5.4444
2.6793
2.6647
2.6568
2.6469
2.6107
2.6050
2.5978
2.5759
2.5650
2.5602
2.5454
2.5216
2.5086
2.5004
2.4865
2.4768
2.4629
2.4579
2.4544
2.4436
2.4313
2.4187
2.4138
2.3912
2.3729
2.3581
2.3345
2.3108
1.4235
1.4139
1.4050
1.2541
0.8795
0.8546
0.8290
0.0000
11
10
9
8
7
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5
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3
2
1
0
ppm
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2.02
1.00
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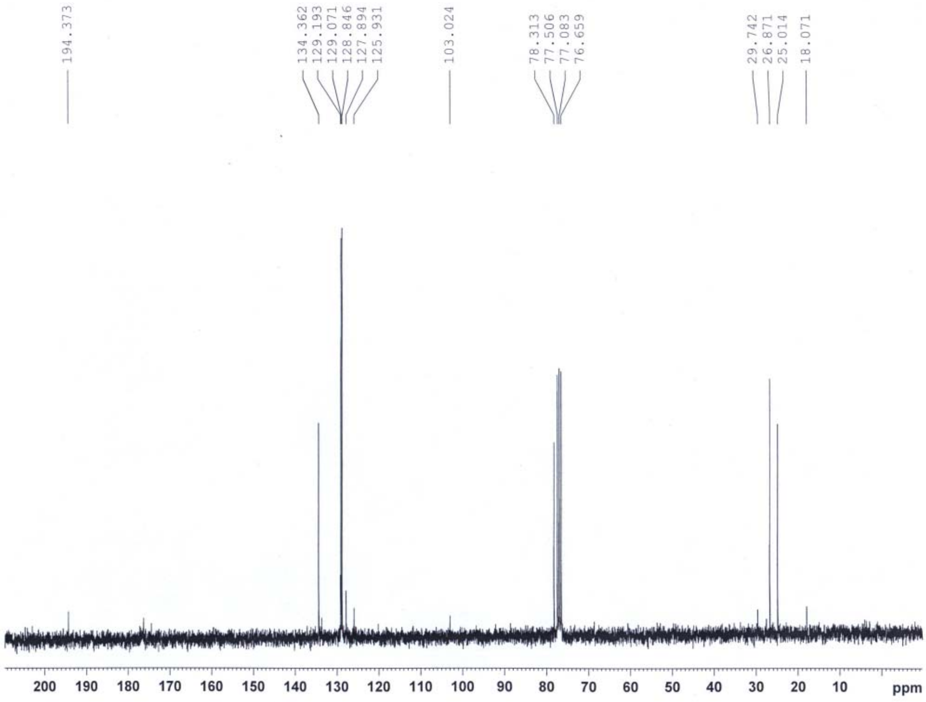
0.67
1.09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29.742
26.871
25.014
18.071
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10
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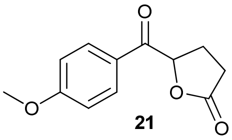
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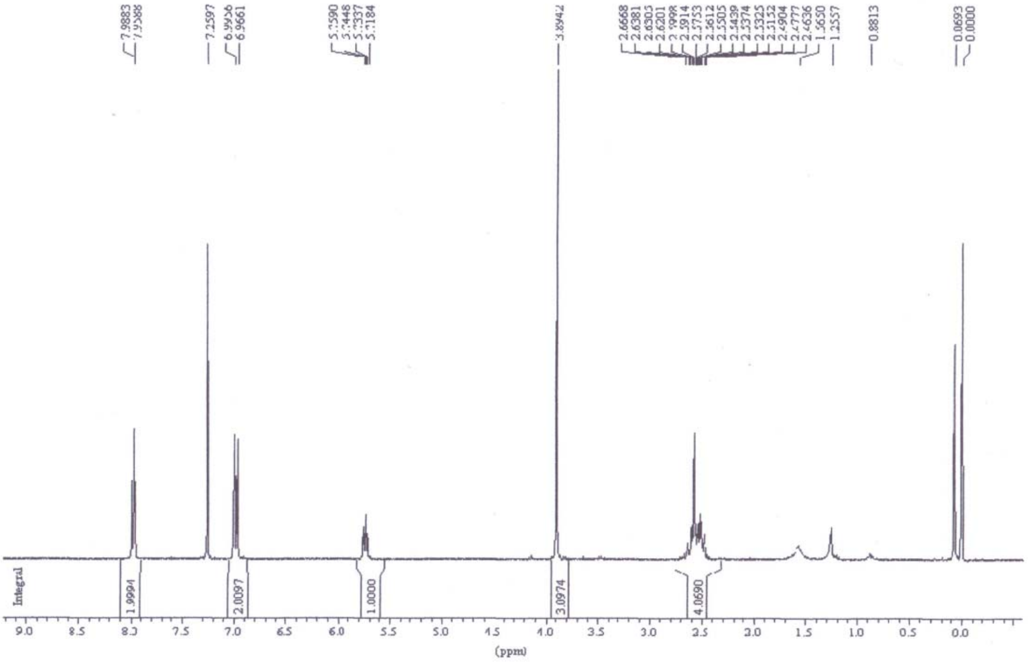
21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5.7337
5.7184
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2.6668
2.6381
2.6305
2.6201
2.5998
2.5914
2.5753
2.5612
2.5505
2.5439
2.5374
2.5325
2.5152
2.4904
2.4777
2.4636
1.5650
1.2557
0.8813
0.0693
0.0000
Integral
1.9994
2.0097
1.0000
3.0974
4.0690
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
2.5
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1.5
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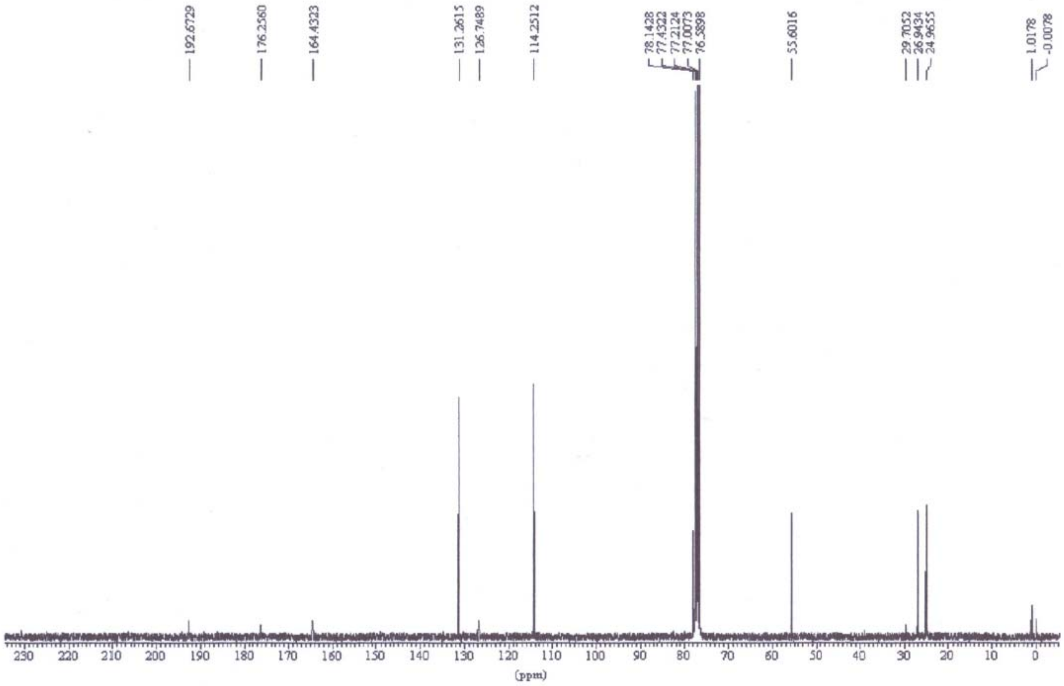
0.5
0.0
(ppm)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126.7489
114.2512
78.1428
77.4322
77.2124
77.0073
76.5898
55.6016
29.7052
26.9434
24.9655
1.0178
-0.0078
230
220
210
200
190
180
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160
150
140
130
120
110
100
90
80
70
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50
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30
20
10
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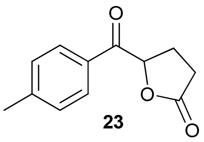
(ppm)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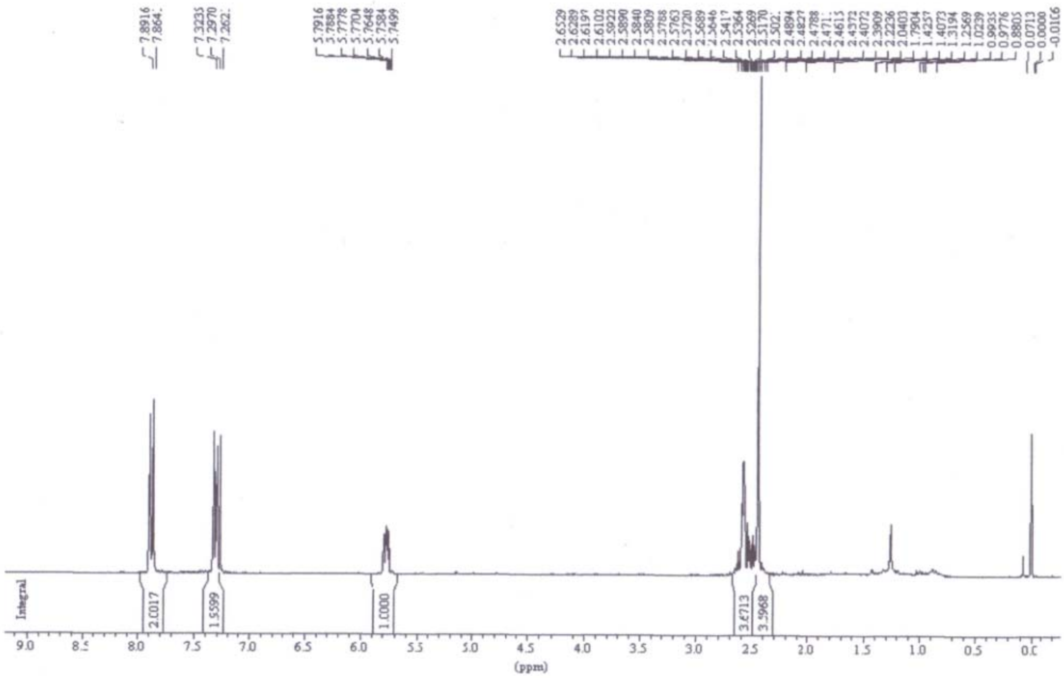
23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7.262
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5.7499
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2.6197
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2.5890
2.5840
2.5809
2.5788
2.5763
2.5720
2.5689
2.5646
2.5417
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2.5269
2.5170
2.502
2.4894
2.4827
2.4788
2.471
2.4615
2.4372
2.4072
2.3909
2.2236
2.0403
1.7904
1.4257
1.4073
1.3194
1.2569
1.0239
0.9935
0.9776
0.8805
0.0713
0.0000
-0.0106
Integral
2.0017
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1.0000
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
2.5
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1.5
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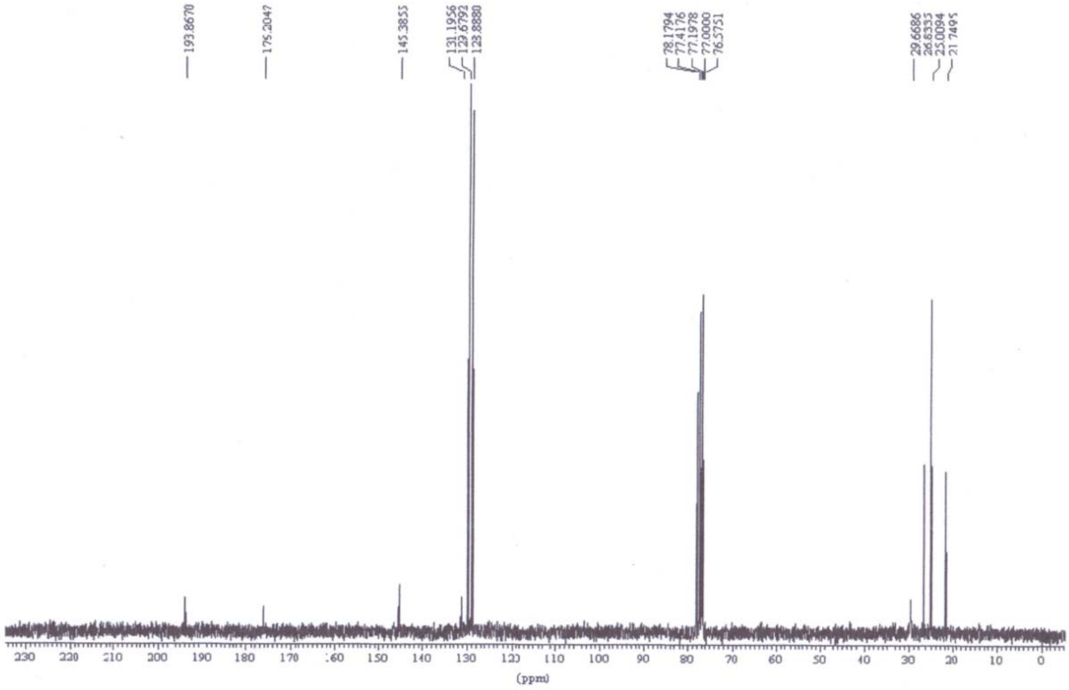
0.0
(ppm)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77.0000
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29.6686
26.8335
25.0094
21.7495
230
220
210
200
190
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120
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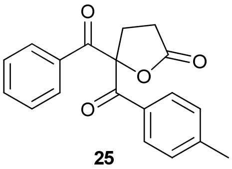
(ppm)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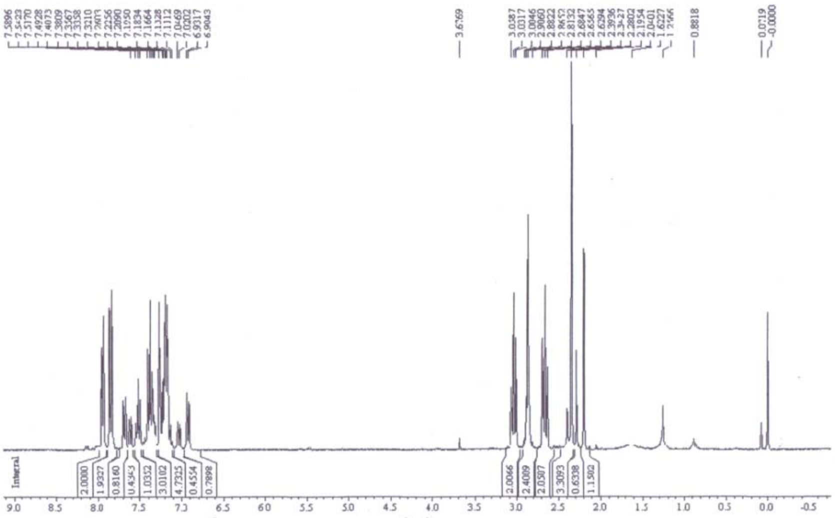
O
O

25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7.3210
7.2073
7.2256
7.2090
7.1950
7.1834
7.1664
7.1328
7.1112
7.0469
7.0202
6.9317
6.9043
3.6769
3.0387
3.0317
3.0046
2.9060
2.8822
2.8652
2.8132
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2.6294
2.3936
2.3427
2.2802
2.1954
2.0401
1.6227
1.2566
0.8818
0.0719
-0.0000
Integral
2.0000
1.9327
0.8160
0.4343
1.0332
3.0102
4.7325
0.4554
0.7898
2.0066
2.4009
2.0587
3.3093
0.6338
1.1502
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
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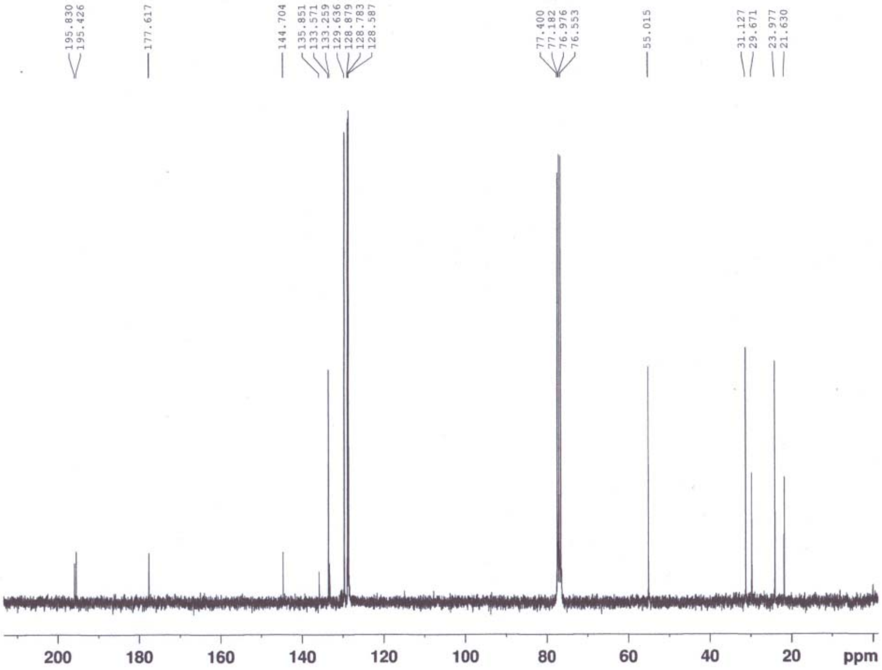
0.0
-0.5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77.182
76.976
76.553
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23.977
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60
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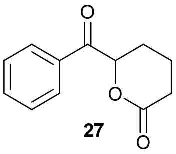
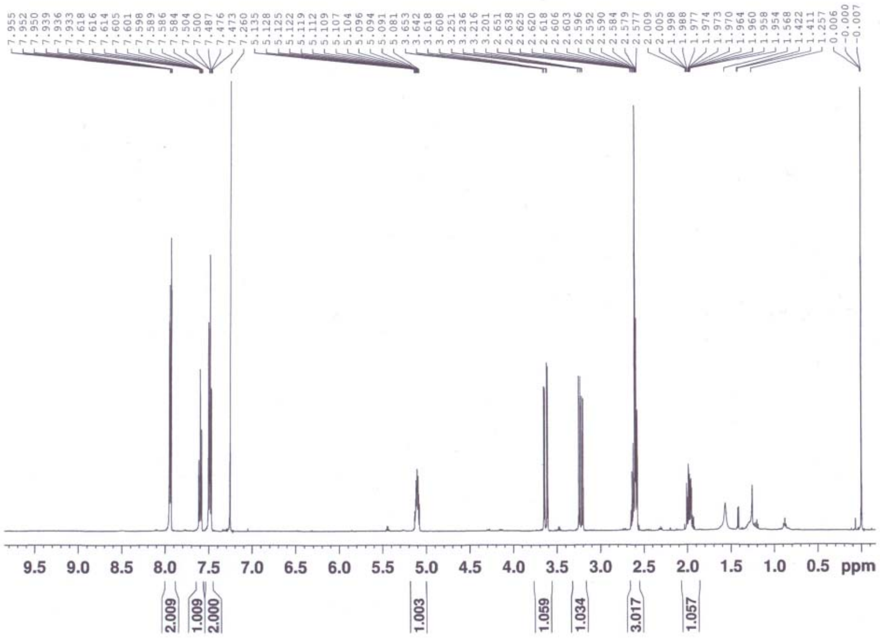
20
ppm



27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7.614
7.605
7.601
7.598
7.589
7.586
7.584
7.504
7.500
7.487
7.476
7.473
7.260
5.135
5.128
5.125
5.122
5.119
5.112
5.109
5.107
5.104
5.096
5.094
5.091
5.081
3.653
3.642
3.618
3.608
3.251
3.236
3.216
3.201
2.651
2.638
2.625
2.620
2.618
2.606
2.603
2.596
2.592
2.590
2.584
2.579
2.577
2.009
2.005
1.998
1.988
1.977
1.974
1.973
1.970
1.964
1.960
1.958
1.954
1.568
1.422
1.411
1.257
0.006
-0.000
-0.007
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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0.5
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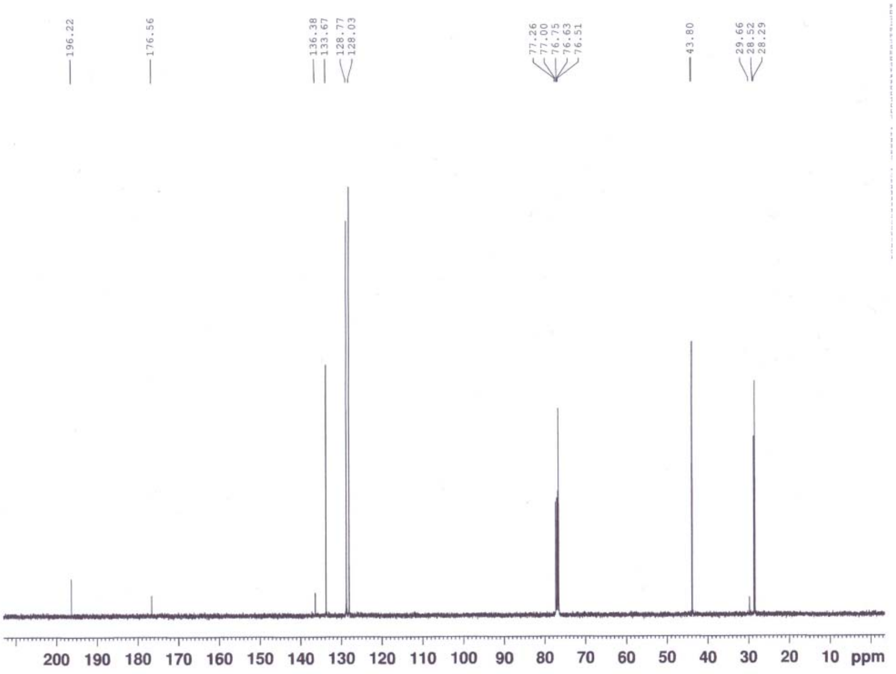
1.057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76.51
43.80
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28.52
28.29
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150
140
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120
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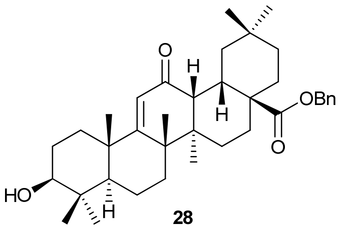
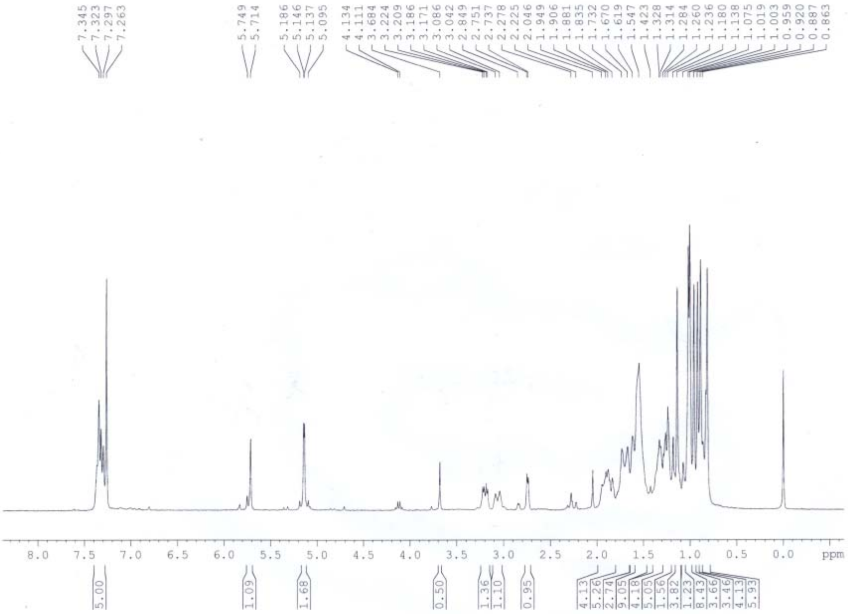
30
20
10
ppm


O
H
H
OBn
O
HO
H

28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5.137
5.095
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4.111
3.684
3.224
3.209
3.186
3.171
3.086
3.042
2.849
2.751
2.737
2.278
2.225
2.046
1.949
1.906
1.881
1.835
1.732
1.670
1.619
1.547
1.423
1.328
1.314
1.284
1.260
1.236
1.180
1.138
1.075
1.019
1.003
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0.920
0.887
0.863
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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1.36
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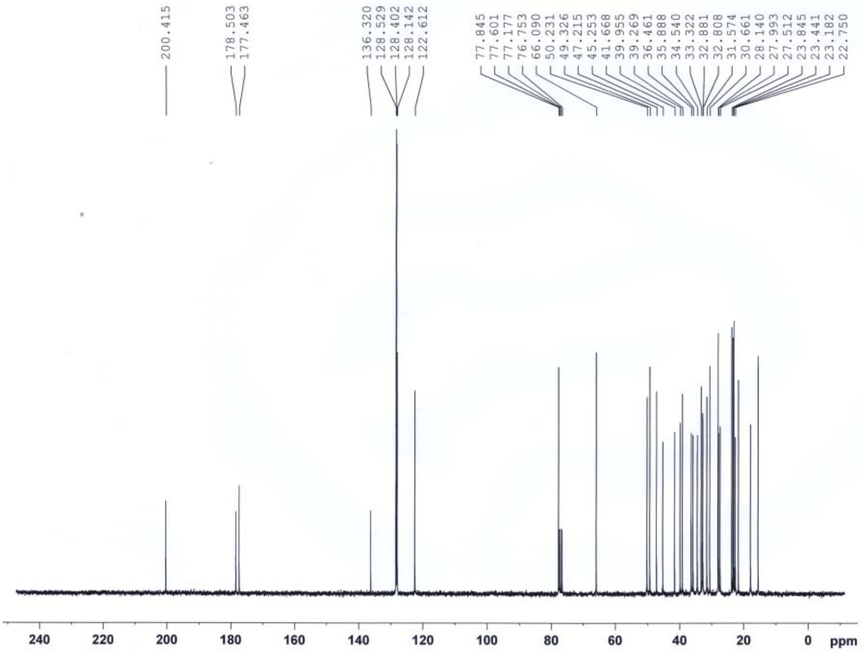
4.13
5.93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47.215
45.253
41.668
39.955
39.269
36.461
35.888
34.540
33.322
32.881
32.808
31.574
30.661
28.140
27.993
27.512
23.845
23.441
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22.750
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120
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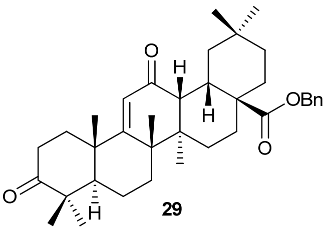
ppm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H
OBn
O
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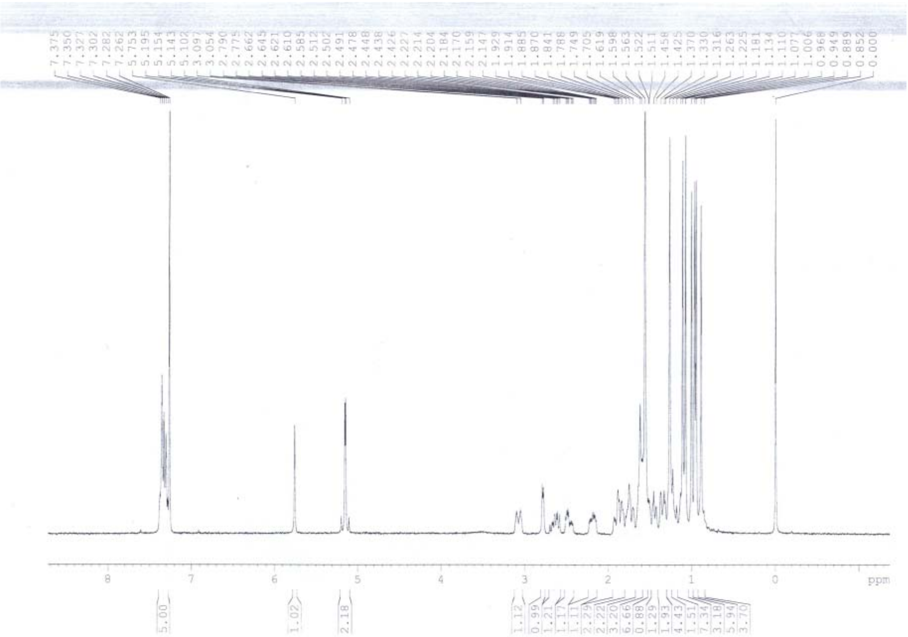
H

29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5.143
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2.775
2.662
2.645
2.621
2.610
2.585
2.512
2.502
2.491
2.478
2.448
2.438
2.426
2.227
2.214
2.204
2.184
2.170
2.159
2.147
1.929
1.914
1.885
1.870
1.841
1.788
1.749
1.705
1.619
1.598
1.563
1.522
1.511
1.458
1.425
1.370
1.330
1.316
1.263
1.225
1.181
1.134
1.110
1.077
1.006
0.968
0.949
0.889
0.852
0.000
9
7
6
5
4
3
2
1
0
ppm
5.00
1.02
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1.12
0.99
1.21
1.17
1.11
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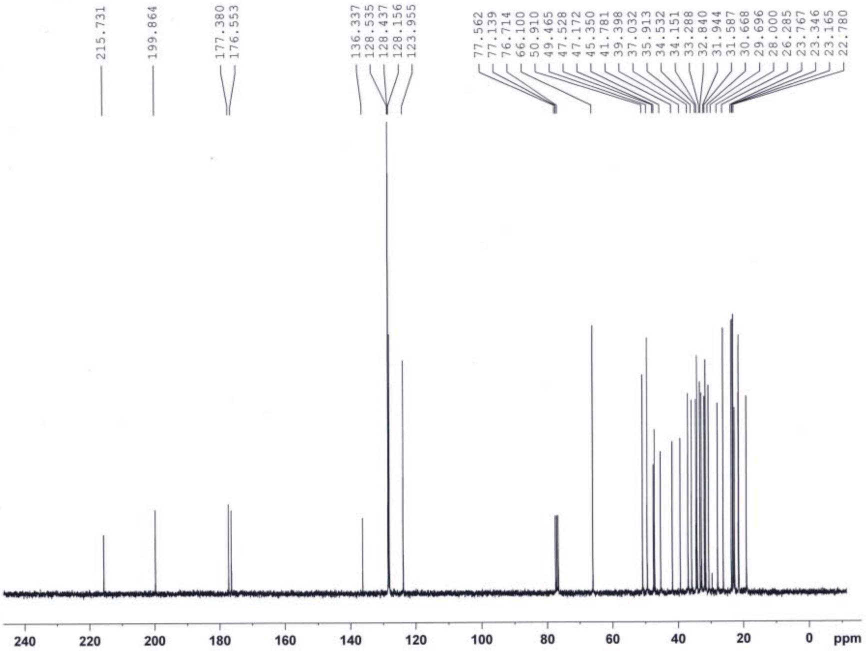
3.70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66.100
50.910
49.465
47.528
47.172
45.350
41.781
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37.032
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34.151
33.288
32.840
31.944
31.587
30.668
29.696
28.000
26.285
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0
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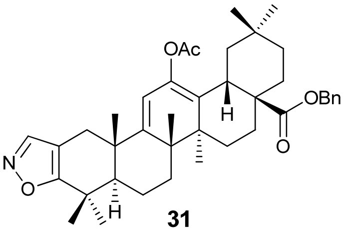
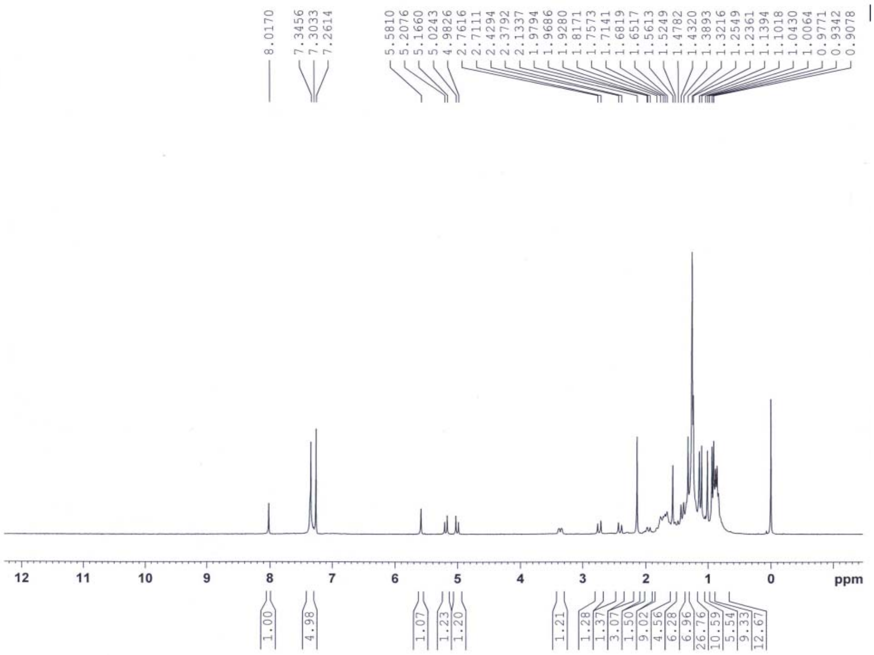

OAc
OBn
O
H
H
N
O

31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4.9826
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2.7111
2.4294
2.3792
2.1337
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1.9686
1.9280
1.8171
1.7573
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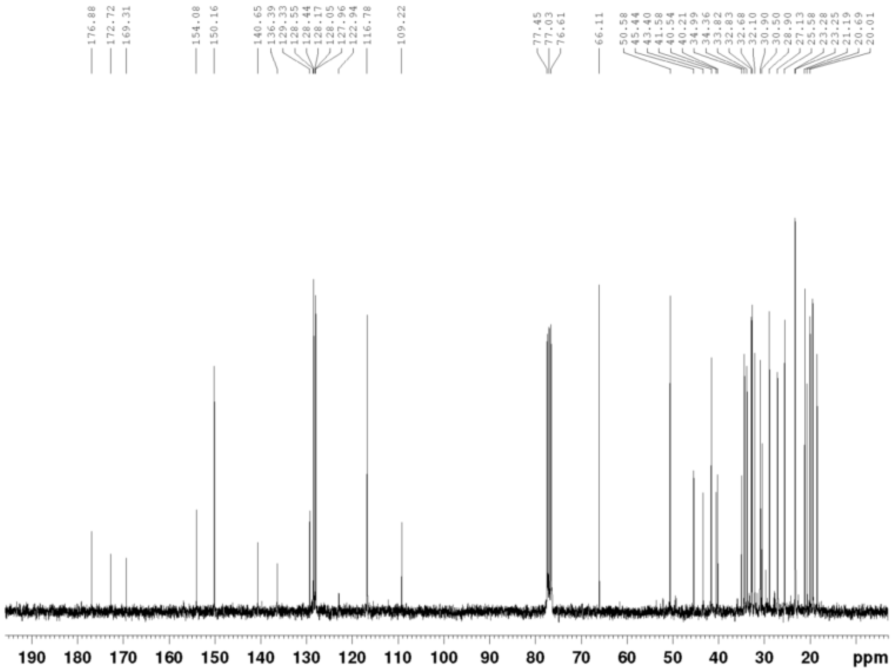
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